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Spontaneous Combustion Susceptibility of U.S. Coals

By J. M. Kuchta, V. R. Rowe, and D. S. Burgess



UNITED STATES DEPARTMENT OF THE INTERIOR

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SPONTANEOUS COMBUSTION SUSCEPTIBILITY OF U.S. COALS

by

J. M. Kuchta,¹ V. R. Rowe,² and D. S. Burgess³

ABSTRACT

The chemical and thermal criteria used for predicting the spontaneous combustion hazard are briefly reviewed and data are presented to characterize the gas desorptions and self-heating tendencies of 29 U.S. coals. Closed vessel desorption experiments showed that CO, CO₂, and CH₄ are the main gases evolved and that the CO, CO/ΔO₂ index, and O₂ absorption rate increase with decreasing rank and increasing oxygen content of the coal. In this Bureau of Mines report, the effects of temperature, moisture, and other variables are discussed together with the application of the data to the complex conditions encountered in a mining environment. An important finding is that the presence of CO alone in a mine is not necessarily an indication of a self-heating reaction of the coal. Based upon experiments conducted in an adiabatic-type calorimeter, the self-heating temperatures of lignite and subbituminous coals can be as low as 30° C, whereas the bituminous coals require a temperature of about 60° C or more. The self-heating hazard is greatest when the coals are dried and exposed to a high humidity condition, apparently as a result of the "heat-of-wetting." Generally, the hazard is greatest with the western coals of the United States.

INTRODUCTION

Coal mine fires due to spontaneous combustion, or self-heating, generally develop by slow oxidation in the coal seams or gob areas and occur most frequently with low-rank coals. Even if an outbreak of fire does not occur, the mining operator may be forced to take drastic action, such as abandonment of an entire mine section. Statistics show that France (15)⁴ and Great Britain (8) each average about seven to eight cases of spontaneous combustion in coal mines each year. In the United States, the incidence

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⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.



rate is somewhat lower even though the number of mines is much greater; one survey for the period from 1952-69 (table 1) indicates that 84 gob fires or less than 10 pct of the total coal mine fires (877) were probably attributable to spontaneous combustion (16). In any case, the future incidence of such fires should be expected to become greater as the mining industry expands and increases its dependence upon coals of lower rank. Such coals are most prevalent west of the Mississippi River in the United States.

TABLE 1. - Statistics of reported coal mine fires during 1952-69¹

Location	Type of fire				Injuries	Fatalities
	Electrical	Frictional	Spontaneous combustion	Total		
Face area equipment..	333	0	0	351	61	20
Conveyor belts.....	27	91	0	134	18	11
Power cables.....	112	0	0	112	13	0
Locomotives.....	38	0	0	38	3	5
Trolley wires.....	57	0	0	57	12	18
Gob areas.....	0	0	65	84	3	3
Miscellaneous.....	35	0	0	101	17	4
Total.....	602	91	65	877	127	61

¹Private communication with Edward M. Kawenski, Mine Safety and Health Administration (MSHA), Pittsburgh, Pa.

The Bureau's recent research in this area has emphasized the development of detection systems (2, 13) and the characterization of the spontaneous combustion tendencies of various U.S. coals (17). Results of the spontaneous combustion work were largely limited to bituminous coals and provided useful guidelines for predicting their self-heating hazard as a function of temperature and of their intrinsic properties; an important finding was that CO formation is not always indicative of self-heating. The prediction of this hazard in a mining environment depends upon the self-heating criterion used and the effects attributable to both the intrinsic nature of the coal and the type of mining or geological condition. This Bureau of Mines report discusses the relative importance of these contributing factors and extends the previously obtained data to other temperature and humidity conditions, particularly to coals of lower rank such as the western subbituminous and lignite grades. The greatest emphasis is upon the reaction of these coals in moist dry air at near-ambient temperature. The reported self-heating temperatures define the minimum or critical temperature above which the coal mass could produce a sustained exothermic reaction under adiabatic conditions.

CRITERIA FOR SPONTANEOUS COMBUSTION

Chemical

The chemical aspects of the spontaneous combustion of coal are not well understood because of the complex compositions of coals and the varied heterogeneous surface reactions that can be involved. It is generally believed that the low-temperature stage of oxidation produces coal-oxygen complexes (19), such as carbonyl and carboxyl compounds, which upon further heating, liberate

CO and CO₂. Thus, the CO or CO₂ emission rates or the corresponding O₂ depletion rates are frequently relied upon as a criterion of coal spontaneous combustion. The Graham index (9), ratio of CO formation to O₂ deficiency (CO/ΔO₂), was proposed for this purpose at the turn of the century and has the practical advantage of being independent of normal ventilation or dilution effects.

Today, CO monitoring systems have been adopted by several sectors of the European community for early detection of spontaneous combustion in coal mines (5, 7). Similarly, a system that provides a measure of the CO/ΔO₂ index has recently been successfully applied by the Bureau to a U.S. mine where this hazard existed.⁵ One complication that can arise in such measurements is that the observed CO may be merely due to the desorption of gases formed during some earlier period, such as the coalification stage, and therefore not indicative of any self-heating. Another complication is that the CO is known to disappear under some conditions (3). Also, the CO/ΔO₂ index can be difficult to analyze when the sampled mine atmosphere has been diluted by ventilation streams of vitiated air, rather than by fresh air. Such uncertainties indicate the need for knowing the background CO or CO index of a mine and the expected variations with ventilation, temperature, or other complicating factors.

Hertzberg⁶ has shown that earlier warning of incipient combustion may be attained for some materials by monitoring submicrometer smoke particulates than by monitoring CO formation. However, the spontaneous combustion of coal is a special case of incipient combustion; CO is released at low temperatures (ambient to 100° C) even in the absence of an incipient fire, whereas smoke particulates are generally formed at higher temperatures. Other material sensing methods, based on changes in mass or composition of the coal, are generally unattractive because of poor sensitivity or impracticality in field operations.

Thermal

Temperature or temperature rise of the reacting coal is the most commonly used criterion of spontaneous combustion. Any temperature rise of the reacting mass is indicative of self-heating, although the exothermic reaction may not be sustained because of conductive or convective heat losses. Assuming heat loss is largely by conduction (q₂) and that the chemical heat release follows the Arrhenius law (q₁), the self-heating rate (q) of a dried coal mass in quiescent air may be expressed as follows:

$$\rho c \frac{\partial T}{\partial t} = \underbrace{\rho Q Z e^{-E/RT}}_{q_1} + \underbrace{\lambda \nabla^2 T}_{q_2} \quad (1)$$

⁵Work cited in reference 2.

⁶Work cited in reference 13.

where ρ is density, c is specific heat, T is temperature, t is time, Q is heat of reaction, Z is rate constant, E is activation energy, R is molar gas constant, λ is thermal conductivity, and ∇^2 is the Laplacian differential operator. Under steady-state conditions, this equation reduces to $q_1 = q_2$, which permits calculation of the self-heating temperature as a function of the size of reactant mass if the chemical kinetic constants (Z and E) are known. These constants can be calculated for the adiabatic case ($q = q_1$) from experimentally determined self-heating rates at various temperatures, as obtained in this report. In the practical cases, allowance must be made for heat losses due to ventilation and moisture evaporation effects and reduced reaction rates due to any oxygen depletion.

The self-heating temperatures of some coals may extend down to near-ambient temperature under adiabatic conditions (11, 14). Under such conditions, Stott (26) reports that the heat evolution can be on the order of 3 cal/cm³ of O₂ absorbed for bituminous coals. Generally, the self-heating rates will increase with increasing temperature and result in increasing CO and CO₂ emission rates. At some elevated temperature, generally between 50° and 100° C, the oxidation rates of all coals will accelerate greatly and ultimately produce smoldering or flaming combustion. Above such critical temperatures, the temperature coefficient of the rate-controlling process appears to increase, as revealed in earlier Bureau studies.

These self-heating temperatures should not be confused with minimum auto-ignition temperatures (AIT's) that are associated with nonadiabatic conditions and much shorter reaction times (a few minutes or less). Under these conditions, the AIT's of coals tend to be about 150° C or more according to Nagy (21), whereas their self-heating temperatures under adiabatic conditions would be expected to be much lower. Comparison of such temperatures is made in this report.

CONTRIBUTING FACTORS OF SPONTANEOUS COMBUSTION

An evaluation of the spontaneous combustion hazard in coal mines requires consideration of the following factors: (1) properties of coal, (2) geological features of coal seams, and (3) mining practices and conditions.

Properties of Coal.--Coals most susceptible to self-heating are characterized by a high pyritic content or by a high intrinsic moisture and oxygen content, as found in the low-rank coals, namely, the subbituminous and lignite grades. The subbituminous- and lignite-grade coals also tend to have a low methane content because of their low degree of coalification and because their internal structure is sufficiently permeable to permit a high level of sorption or desorption. The reactivity of these coals, including oxidation and CO emission, is greatest when the coals are finely divided and dried.

For coals capable of self-heating, the heat evolved can be as much as 2½ times greater for exposures in moist air than in dry air, and the heat of wetting itself can be greater than the heat of oxidation.⁷ Van Krevelen (29)

⁷Works cited in references 11, 14, and 26.

states that the heat of wetting can be assumed to be about $1 \text{ cal}/10 \text{ m}^2$ of internal surface of a carbonaceous solid. Such moisture effects are particularly important where the coal is subject to "weathering." Any heating by condensation, oxidation, or sorption processes can be expected to be a strong function of the permeability, particle size, and surface area of the coal mass. The permeability and internal surface area will vary with the petrographic components of the coal. Agroskin (1) claims that a coal with a high fusain content is most favorable for adsorption of oxygen at low temperatures because of the fibrous structure. However, the adsorption of gases decreases with increasing temperature, whereas the oxidation process is accelerated, indicating the less fibrous structures of coal (vitrain and clarain) may exert the greater influence on oxidation at high temperatures. Most data indicate that coals with a high vitrain content are more susceptible to self-heating than others.

Other coal properties such as specific heat and thermal conductivity are primarily important in determining heat loss limitations in a reacting mass. They are particularly sensitive to the porosity and moisture content.

Geological Features of Coal Seams.--The geological features of a coal seam, like the specific coal properties, are factors that cannot be controlled to prevent spontaneous combustion. This includes the geometrical and physical features of both the coal seam and adjacent rock strata. A complete summary of the important features is given in a comprehensive report by Soviet investigators (31) and in the previously cited reports of French and Canadian investigators.⁸ The main features that enhance the susceptibility of coals to spontaneous combustion are thick or multiple coal seams, highly pitched seams, weak or disturbed strata, and coal seams with faults or shallow overburden. According to Soviet investigators, coal seams less than 1.5 m thick appear to pose the least hazard and coal seams greater than 3 m thick pose the greatest hazard. In the United States, the thickest seams are found in the Rocky Mountains where some seams are up to at least 15 m thick, as opposed to less than 3 m in the Appalachian Mountains. Since tectonic disturbances were greatest in the Rocky Mountain region, the coal seams in this area are the most likely to be steeply pitched and to contain faults or cavings. All of these geological factors contribute to the development of fissures which increases the air leakage needed to promote any combustion.

Geothermal anomalies in the given strata may also produce heating to conceivably initiate spontaneous combustion of a coal seam. However, although such heating has been suspected as a possible cause of a few fires in western U.S. mines, the evidence has not been conclusive.

Mining Practices and Conditions.--Mining itself requires disturbing the coal seam and adjacent strata and, therefore, can produce conditions that are favorable for initiating spontaneous combustion. These conditions depend greatly upon the mining method and the ventilation provided to the mined or unmined coal. In longwall mining, the retreating method is less hazardous than the advancing method because the retreating method requires ventilation

⁸Works cited in references 8 and 15.

of roadways along an unmined panel, whereas the advancing method involves ventilation beside the mined out or caved panel (gob area) across which air leakage can readily occur. The optimum air leakage flows for self-heating are rather low, the minimum predicted velocity being on the order of 5 cm/min for beds of coarse coal (minus 3-mesh) (27). Balancing the pressure across the mine roadways is one means of minimizing the air leakage although this is not practical in the working areas.

In room-and-pillar mining, the self-heating hazard is similarly related to those conditions that result in optimal air leakages through a permeable mass of coal; gob areas are again the most suspect. Although the gob areas are normally "sealed" off, it is often not possible to make the gobs air-tight because of faults or permeability of the surrounding strata; thus, the air leakage can be sufficient to sustain oxidation and promote a coal gob fire. In the case of coal pillars or other solid sections of coal, the leakage paths develop as a result of mining stresses or tectonic disturbances; some frictional heating can also be expected when fissured or pulverized layers are formed by this action. In all cases, the self-heating hazard will be greatest for those ventilation conditions that insure a sufficient supply of oxygen to the reacting mass without excessive removal of the heat generated.

EXPERIMENTAL APPARATUS AND PROCEDURES

Desorption Experiments

The various coals were exposed to dry air at ambient temperature (25° C) to characterize their gas emissions and oxygen uptakes. The coal samples were crushed and classified in a glove box and stored in a nitrogen atmosphere prior to use. Most of the experiments were made in a 250-ml vessel with 50-g samples of freshly ground coal of 10 to 20 mesh (0.2 to 0.085 cm). The mass of atmospheric oxygen in the 250-ml vessel (about 0.05 g) was generally insignificant relative to the several weight-percent of oxygen initially present in the coal. The procedure consisted of sealing the sample in an Erlenmeyer flask equipped with a pressure transducer and sampling the gases for extended periods to determine the CO, CO₂, and CH₄ emissions and the O₂ absorption; the gas samples were withdrawn through a vessel port by a hypodermic syringe. The gases were analyzed by conventional gas chromatographic methods that could detect CO concentrations down to 5 ppm and O₂ differences of 500 ppm or more. These experiments were made with both dried and undried coal samples; here, dried coals refer to samples previously exposed to flowing nitrogen at 70° C for about 24 hours, which reduced the intrinsic moisture content to a few percent or less.

Similar experiments were also made in a simulated air atmosphere of 79 pct argon and 21 pct ¹⁸O₂ isotope to determine whether the CO and CO₂ emissions are attributable to ongoing oxidation of the coal sample. Argon was preferred to nitrogen because the latter has the same mass as C¹⁶O and, therefore, its use would increase the analytical uncertainties. For these experiments, a 110-ml cylindrical glass reaction tube was fabricated with an O-ring joint to permit easy loading and wrapped with a heating tape for varying the temperature. The reaction vessel was connected to a vacuum and gas

transfer system and pressure instrumentation, including a McLeod gage for vacuum measurements and a strain gage pressure transducer for monitoring total pressure changes. All coal samples were prepared and stored in an argon atmosphere, using a glove box as in the previous test phase. Here, the experiments were made with an ~25-g sample of 10- to 20-mesh coal unless otherwise noted. The sample was loaded in the reaction cell, evacuated, and exposed to the simulated air for periods of up to 1 week. Gas samples were withdrawn into 10-ml sampling bulbs at various time intervals to examine the desorption or oxidation products. For experiments at elevated temperatures, the loaded reaction cell was placed in an oven at the desired temperature and heated for various time intervals before transferring the reaction cell back to the kinetics rack for sampling the reaction products.

Gas samples in the isotope tracer experiments were analyzed by gas chromatography and mass spectrometry using both low- and high-resolution techniques. These analyses included total concentrations of O_2 , CO, and CO_2 and the isotopic distributions of each of these gases. The isotopic purity of the $^{18}O_2$ was between 95 and 99 at. pct, and $^{18}O^{16}O$ was the major impurity.

Self-Heating Experiments

The self-heating tendencies of the coals were studied in an adiabatic calorimeter. Figure 1A is a schematic of the adiabatic heating apparatus and figure 1B shows the apparatus in operation. This apparatus is designed to maintain the coal and its immediate surroundings (oven) at the same temperature during at least the incipient stage of combustion. With such control of temperature ($\Delta T = 0$), the self-heating rate should follow that predicted by equation 1 for the adiabatic case ($q_2 = 0$). The calorimeter consists of an insulated oven chamber with three separate heaters, a 15-cm-diam Dewar vessel containing a sample oven (middle heater), and a stainless steel wire sample basket (7.6 cm in diameter by 7.6 cm high) suspended by a wire strand. Pre-heated air is brought into the calorimeter by passing it through an externally heated line and the outer oven; the air enters near the bottom and slowly circulates up around the sample with the help of a magnetically controlled fan (<5 rpm). Iron-constantan thermocouples are installed at various locations, three of which are shown in figure 1A, for determining the sample and oven temperatures; sample-oven differential thermocouples were used for control purposes and for detection of self-heating. All thermocouples were simultaneously calibrated.

Thermocouple outputs were fed to an instrument console that was equipped with solid-state electronic components for programing the heating and for monitoring or controlling the sample and oven temperatures. These outputs were recorded continuously on millivolt recorders and spot-checked by use of a digital differential voltmeter. This system was sufficiently sensitive to detect temperature differences as small as $0.02^\circ C$ and had a drift rate from electronic instability of about 0.05° per hour at $50^\circ C$. The calorimeter is also equipped with a load cell for monitoring sample weight changes but which was not sufficiently sensitive for work where mass changes due to reaction were very small.

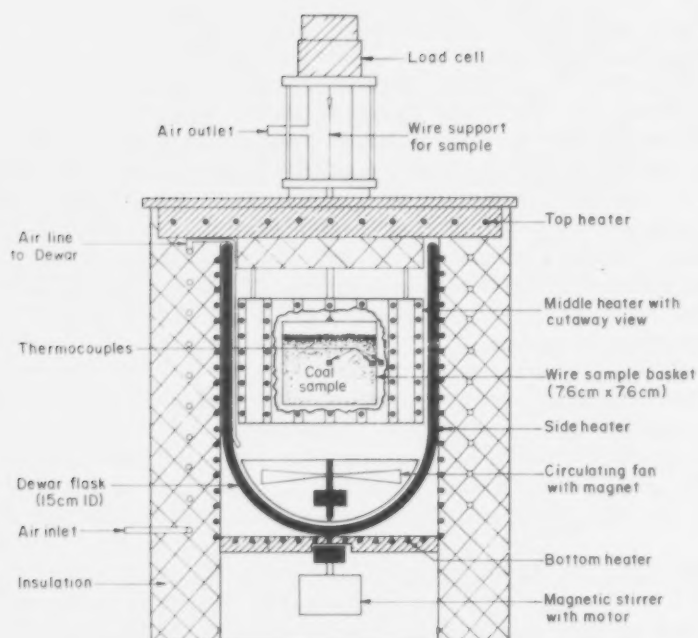


FIGURE 1A. - Schematic of adiabatic heating apparatus.

Experiments were made with both dried and undried 100-g samples of freshly ground coals; the particle size was either 50 to 70 mesh or 100 to 200 mesh. The 100 to 200 particle size samples were used for most of the present determinations. The sample was placed in the calorimeter and brought to the test temperature (set point) in a stream of flowing nitrogen, at which time the sample and oven (inner) temperatures agreed to within 0.1°C . Subsequently, the calorimeter is put into an automatic control mode and the sample is exposed to a flowing stream of dry or moist air for a period of at least 24 hours, unless self-heating occurs earlier. An air flow



FIGURE 1B. - Adiabatic heating apparatus.

rate of 50 cm³/min has been found optimum for self-heating in this apparatus. The sample temperature is varied to define the minimum temperature for self-heating, as evidenced by a significant temperature rise of the sample. In these determinations, the automatic temperature controls must be carefully adjusted to insure that the observed temperature rise is not attributable to any "boot strapping" effect by systematic deviations of the oven temperature controls. Thus, it is important that the sample oven temperature does not exceed the sample temperature during any self-heating.

RESULTS AND DISCUSSION

Coal Analyses

Proximate and ultimate analyses were obtained for all coal samples investigated in this work (table 2). The oxygen contents should be considered as relative values since they were determined by the difference technique. The heating values were calculated by applying the following formula:

$$Q = 14.54C + 62.03 (H-O/8) + 4050S, \quad (2)$$

where Q is the heating value in British thermal units per pound and C, H, O, and S are the element constituents in weight fractions; the conversion factor for metric equivalents is 0.556 cal/g.

Table 2 presents the analyses obtained for the different coals, including lignite, subbituminous, and bituminous. The coals are listed in an increasing order of calorific values (as received basis) which essentially corresponds to their approximate classification by rank. As expected, the moisture and oxygen contents of the as received samples are greatest for the lignites and generally decrease with the increased rank of the coal. The increased rank is also reflected by an increased carbon content, whereas no apparent correlation exists with volatile content, although the Pocahontas coal stands out as the least volatile. Most of the coals were low sulfur content, only a few exceeding 2.5 wt-pct, namely those from the Prince (Nova Scotia, Canada), Allison (Ohio) and (Napoleon (Ohio) mines. Based upon these data, the three classes of coal samples may be characterized as shown in table 3.

Exposure of Coals to Air in Closed Vessels

Gas Emissions--CO, CO₂, and CH₄

The gas emissions of over 25 coals were determined in the closed vessel experiments in air at ambient temperature. The main gases evolved were CO, CO₂, and CH₄ which varied with exposure time or O₂ consumption and the composition, dryness, and particle size of coal. Generally, the CO emissions increased linearly with time up to certain concentration levels after which they leveled off or were less time-dependent as the O₂ in the vessel became greatly depleted. The CO₂ and CH₄ emissions also increased with exposure time but the data trends were not necessarily the same as those for CO.

TABLE 2. - Analyses of coals as received

Mine	Location	Heating value, Btu/lb	Proximate analysis, wt-pct				Ultimate analysis, wt-pct					
			Mois- ture	Volatile matter	Fixed carbon	Ash	Hydro- gen	Car- bon	Nitro- gen	Oxy- gen	MAFI	Sul- fur
LIGNITE												
Beluga.....	Alaska.....	7,000	24.5	31.1	28.9	15.5	5.9	42.0	0.7	35.8	23.3	0.1
Gascoyne strip.....	N. Dak.....	7,150	34.0	29.5	30.2	6.3	6.7	43.0	.8	41.9	19.6	1.3
Husky strip.....	N. Dak.....	7,280	34.1	30.7	29.0	6.2	7.0	42.7	.6	42.8	20.9	.6
Monticello.....	Tex.....	7,430	29.4	31.9	27.7	11.0	6.4	43.3	1.2	37.6	19.2	.6
Center strip.....	N. Dak.....	7,660	32.0	32.5	30.9	4.6	6.7	46.1	.7	41.5	20.6	.4
Darco strip.....	Tex.....	7,850	31.1	30.5	32.5	5.9	6.6	46.1	.8	39.7	19.1	1.0
Sandow strip.....	Tex.....	8,940	21.1	39.5	29.1	10.3	6.4	50.8	.9	30.6	17.3	1.0
SUBBITUMINOUS												
Sarpy Creek, Rosebud	Mont.....	9,330	22.0	32.5	39.4	6.1	6.2	54.6	0.7	31.9	17.2	0.5
Sarpy Creek, stray No. 2.	Mont.....	9,460	18.5	33.5	37.8	10.2	5.9	54.5	.7	27.9	16.1	.8
Dravo, seam No. 82...	Wyo.....	10,620	14.7	33.0	47.7	4.6	5.8	61.7	1.4	25.6	15.7	.9
Jim Bridger.....	Wyo.....	10,740	15.7	31.6	49.9	2.8	5.8	62.6	1.0	27.4	16.4	.4
P&M, Mammoth.....	Mont.....	11,130	11.2	38.2	46.9	3.7	5.4	65.9	1.1	23.5	16.0	.4
Dravo, seam No. 80..	Wyo.....	11,190	11.7	38.0	46.9	3.4	6.0	64.1	1.7	24.2	16.2	.6
BITUMINOUS												
Sunnyhill No. 9.....	Ohio.....	11,520	8.2	35.9	46.3	9.6	5.4	65.5	1.3	15.7	10.2	2.5
Inland No. 6.....	Ill.....	12,370	6.2	30.5	55.4	7.9	5.2	70.8	1.6	14.0	9.8	.5
Prince.....	Nova Scotia	12,580	3.2	35.1	52.4	9.3	4.9	69.7	1.3	10.1	8.2	4.7
Sahara No. 21.....	Ill.....	12,650	4.5	32.7	54.2	8.6	5.2	71.1	1.5	11.2	8.2	2.4
Sahara No. 20.....	Ill.....	12,760	6.5	33.8	52.4	7.3	5.2	71.5	1.6	12.3	7.5	2.1
Napoleon.....	Ohio.....	12,830	6.2	43.3	45.1	5.0	5.7	70.6	1.4	14.2	9.8	3.1
Sunnyside No. 1.....	Utah.....	13,060	4.7	37.4	53.2	4.7	5.5	73.5	1.5	13.6	10.3	1.2
Somerset No. 2.....	Colo.....	13,250	2.7	37.6	53.7	6.0	5.4	74.4	1.5	12.2	10.7	.5
Somerset No. 1.....	Colo.....	13,770	3.8	39.1	54.2	2.9	5.8	76.5	1.6	12.6	9.9	.6
York Canyon.....	N. Mex.....	13,680	1.4	35.9	53.9	8.8	5.3	75.7	1.6	8.2	7.6	.4
Allison.....	Ohio.....	13,660	2.5	43.5	46.3	7.7	5.4	73.2	1.3	7.1	5.6	5.3
Powhatan No. 3.....	Ohio.....	13,690	2.9	41.5	50.7	4.9	5.6	76.3	1.7	9.2	7.1	2.3
Vail.....	Ohio.....	13,780	4.1	41.2	50.3	4.4	5.6	75.6	1.6	10.2	7.3	2.6
Scotia.....	Ky.....	13,850	1.6	35.1	54.1	9.2	5.1	76.0	1.2	7.9	7.3	.6
Bruceton.....	Pa.....	14,500	1.5	38.9	55.8	3.8	5.6	79.7	1.8	7.9	6.9	1.2
Pocahontas No. 3....	W. Va.....	14,360	2.7	16.3	75.9	5.1	4.5	84.1	1.1	4.6	2.6	.6

MAF Moisture-ash free.

TABLE 3. - Composition range for three classes of coals as received

Sample	Lignite	Subbituminous	Bituminous
Moisture.....wt-pct..	20-35	10-25	1-10
Volatiles.....wt-pct..	30-40	30-40	15-45
Fixed carbon.....wt-pct..	25-35	35-50	45-75
Oxygen.....wt-pct..	30-45	20-30	5-15
Heating value.....Btu/lb..	7-9,000	9-11,000	11-15,000
Heating value.....cal/g..	4-5,000	5-6,000	6-8,300

Figure 2 shows the desorption data obtained with 50-g samples of 10- to 20-mesh Bruceton bituminous coal in a 250-ml vessel. Note that the CO emission closely follows the O₂ reduction and is noticeably greater for the predried sample (N₂ at 70° C) than the undried sample. In comparison, the CO₂ tends to become saturated earlier and is much greater for the undried sample, just the opposite of that of the CO emission. The CH₄ emission (not shown) was also greater with an undried coal. These data suggest that CO₂ is more loosely held than CO within the coal but that upon thermal drying the CO formation is enhanced, apparently due to some partial oxidation of the coal or

greater ease of diffusion by the CO species. Thus, dried samples should be relied upon to obtain the most conservative estimate of the CO formation of coals at ambient temperature.

Similar data trends were found in experiments with ground samples of other coals, although their desorption rates varied with the coal rank. Table 4 summarizes the gas desorption data obtained for both dried and undried samples of various U.S. coals after an exposure period of 7 days. As in table 2, the descending order of coals is approximately in order of increasing rank. Data are included from earlier Bureau work in which the coal particle size was larger (minus 3-mesh) than that (10 to 20 mesh) used in the present work. Although such particle size differences can affect the desorption rates, they did not have a large effect upon the final ratio of CO formation to oxygen reduction (CO index).

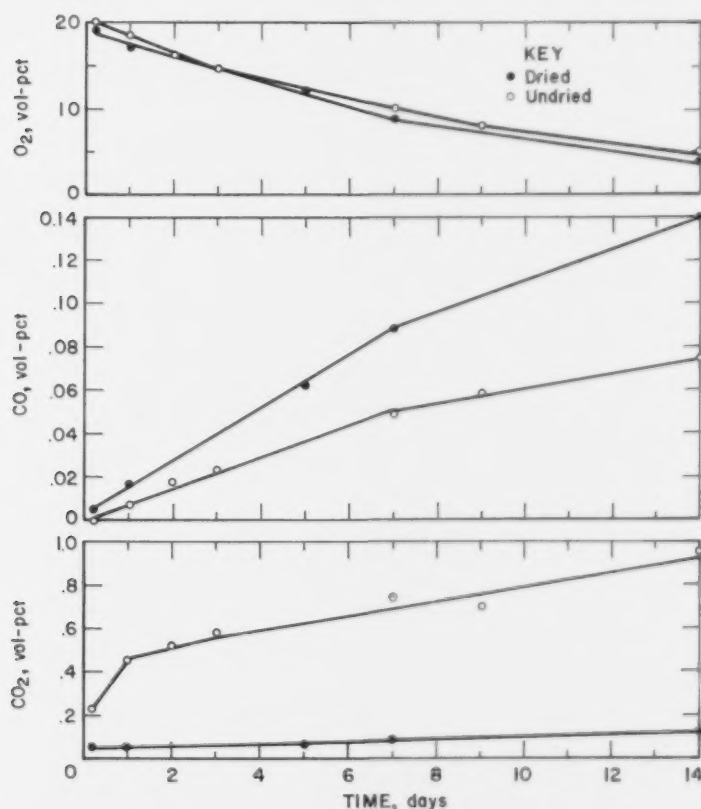


FIGURE 2. - CO and CO₂ formation and O₂ depletion versus time in closed vessel experiments with 10- to 20-mesh dried and undried Bruceton coal in air at 25° C.

TABLE 4. - Gas emissions by ground coals in closed vessel experiments, 7 days

(Sample loading--50 g in 250-ml vessel; particle size--10 to 20 mesh)

Mine	Location	CH ₄ , vol-pct	O ₂ , vol-pct	CO ₂ , vol-pct	CO, vol-pct	CO, CO ₂ , vol-pct/vol-pct	CO, ΔO ₂ , ppm/vol-pct
LIGNITE							
Undried coal							
Beluga.....	Alaska.....	0.001	0.76	2.90	0.230	0.080	114
Gascoyne strip.....	N. Dak.....	.002	.60	5.20	.400	.077	197
Husky strip.....	N. Dak.....	.001	7.15	3.00	.220	.073	160
Monticello.....	Tex.....	ND	ND	ND	ND	ND	ND
Center strip.....	N. Dak.....	ND	ND	ND	ND	ND	ND
Darco strip.....	Tex.....	.001	3.33	3.00	.160	.053	91
Sandow strip.....	Tex.....	.001	10.10	3.20	.200	.063	185
Dried coal							
Beluga.....	Alaska.....	0.001	2.70	0.250	0.370	1.44	198
Gascoyne strip.....	N. Dak.....	.001	2.90	.013	.440	33.85	244
Husky strip.....	N. Dak.....	.002	.99	.160	.490	3.06	246
Monticello.....	Tex.....	.002	.47	.450	.390	.87	191
Center strip.....	N. Dak.....	.002	.85	.420	.430	1.02	215
Darco strip.....	Tex.....	.001	1.40	3.500	.380	.11	195
Sandow strip.....	Tex.....	.001	1.61	.020	.440	22.00	228
SUBBITUMINOUS							
Undried coal							
Sarpy Creek, Rosebud....	Mont.....	0.001	1.90	1.40	0.290	0.207	153
Sarpy Creek, stray No. 2	Mont.....	.015	3.30	2.80	.300	.107	170
Dravo, seam No. 82.....	Wyo.....	.001	1.00	.92	.240	.261	121
Jim Bridger.....	Wyo.....	<.001	14.30	.67	.100	.149	152
P&M Mammoth.....	Mont.....	.001	15.50	.87	.130	.150	241
Dravo, seam No. 80.....	Wyo.....	.003	6.10	2.10	.220	.105	149
Dried coal							
Sarpy Creek, Rosebud....	Mont.....	0.001	0.72	0.020	0.360	17.82	178
Sarpy Creek, stray No. 2	Mont.....	.010	.57	.170	.440	2.59	216
Dravo, seam No. 82.....	Wyo.....	.002	.90	.200	.500	2.50	250
Jim Bridger.....	Wyo.....	.002	2.85	.100	.340	3.40	188
P&M Mammoth.....	Mont.....	<.001	11.30	.230	.280	1.22	292
Dravo, seam No. 80.....	Wyo.....	.002	7.90	.210	.370	1.76	285
BITUMINOUS							
Undried coal							
Sunnyhill No. 9.....	Ohio ¹	0.29	6.40	0.36	0.110	0.306	76
Inland No. 6.....	Ill. ¹	.60	13.10	.40	.110	.275	141
Prince.....	Nova Scotia	.001	17.40	.57	.038	.067	108
Sahara No. 21.....	Ill. ¹	.45	13.80	.26	.058	.223	82
Sahara No. 20.....	Ill. ¹	14.80	.70	.88	.061	.069	30
Napoleon.....	Ohio ¹	.01	9.30	1.20	.065	.054	56
Sunnyside No. 1.....	Utah ¹	.02	19.50	.19	.025	.132	179
Somerset No. 2.....	Colo. ¹	.81	12.80	.31	.100	.323	124
Somerset No. 1.....	Colo.....	ND	ND	ND	ND	ND	ND
York Canyon.....	N. Mex.....	1.95	17.70	.27	.051	.189	159
Allison.....	Ohio ¹	1.27	17.40	.30	.012	.040	34
Powhatan.....	Ohio ¹	.93	16.80	.64	.020	.031	49
Vail.....	Ohio ¹	.87	15.50	.45	.013	.093	77
Scotia.....	Ky.....	1.00	8.50	.66	.036	.055	29
Bruceton.....	Pa.....	.28	10.00	.74	.049	.066	45
Pocahontas No. 3.....	Wyo. ¹	7.00	10.20	.41	.024	.057	22
Dried coal							
Sunnyhill No. 9.....	Ohio ¹	0.001	6.30	0.200	0.160	0.80	110
Inland No. 6.....	Ill. ¹	ND	ND	ND	ND	ND	ND
Prince.....	Nova Scotia	.001	14.74	.160	.110	.69	179
Sahara No. 21.....	Ill. ¹	ND	ND	ND	ND	ND	ND
Sahara No. 20.....	Ill. ¹	.540	1.00	.020	.150	7.50	75
Napoleon.....	Ohio ¹	ND	ND	ND	ND	ND	ND
Sunnyside No. 1.....	Utah ¹	.001	17.50	.220	.060	.27	178
Somerset No. 2.....	Colo. ¹	ND	ND	ND	ND	ND	ND
Somerset No. 1.....	Colo.....	.040	4.10	.130	.200	1.53	119
York Canyon.....	N. Mex.....	.023	16.90	.037	.052	1.41	131
Allison.....	Ohio ¹	ND	ND	ND	ND	ND	ND
Powhatan.....	Ohio ¹	ND	ND	ND	ND	ND	ND
Vail.....	Ohio ¹	ND	ND	ND	ND	ND	ND
Scotia.....	Ky.....	.033	11.10	.035	.047	1.33	48
Bruceton.....	Pa.....	.061	8.80	.082	.089	1.09	74
Pocahontas.....	Wyo. ¹	2.90	16.80	.210	.027	.13	66

ND Not determined for the indicated dried or undried coal samples.

¹Particle size of minus 3-mesh.

Generally, the CO and CO₂ emissions and the O₂ absorptions were greatest for the lower ranked coals, although the data were not entirely consistent with their order of ranking. The uncertainties in obtaining and preparing a representative mine sample can account for most of the inconsistencies; for example, samples taken from various parts of a given coal seam can vary in composition and, therefore, can yield different levels of CO and CO₂. Consistent with figure 2, the levels of CO₂ are greater than CO for undried coals, whereas except for a few the opposite is found for dried coals. The same trend would be expected from the weathering of coals during their storage or transportation. Figure 3 shows that the CO formation is a strong function of the intrinsic moisture and oxygen (moisture-ash free, MAF) content of the coal. The data are for dried samples and show that CO formation correlates inversely with the rank of coal. A CO concentration of about 0.25 vol-pct or 0.5 cm³ CO per 50 g of coal appears to be the critical value for distinguishing between the bituminous coals and the more reactive lignite and subbituminous coals; the corresponding value for undried samples of coal is about 0.1 vol-pct or 0.2 cm³ per 50 g of coal. In the application of these data, only the relative differences for the coals are significant since the measurements reflect only the residual CO, CO₂, and CH₄ after crushing.

The lower rank coals were also characterized by CH₄ desorptions that were barely detectable (table 4). For both dried and undried samples, the CH₄

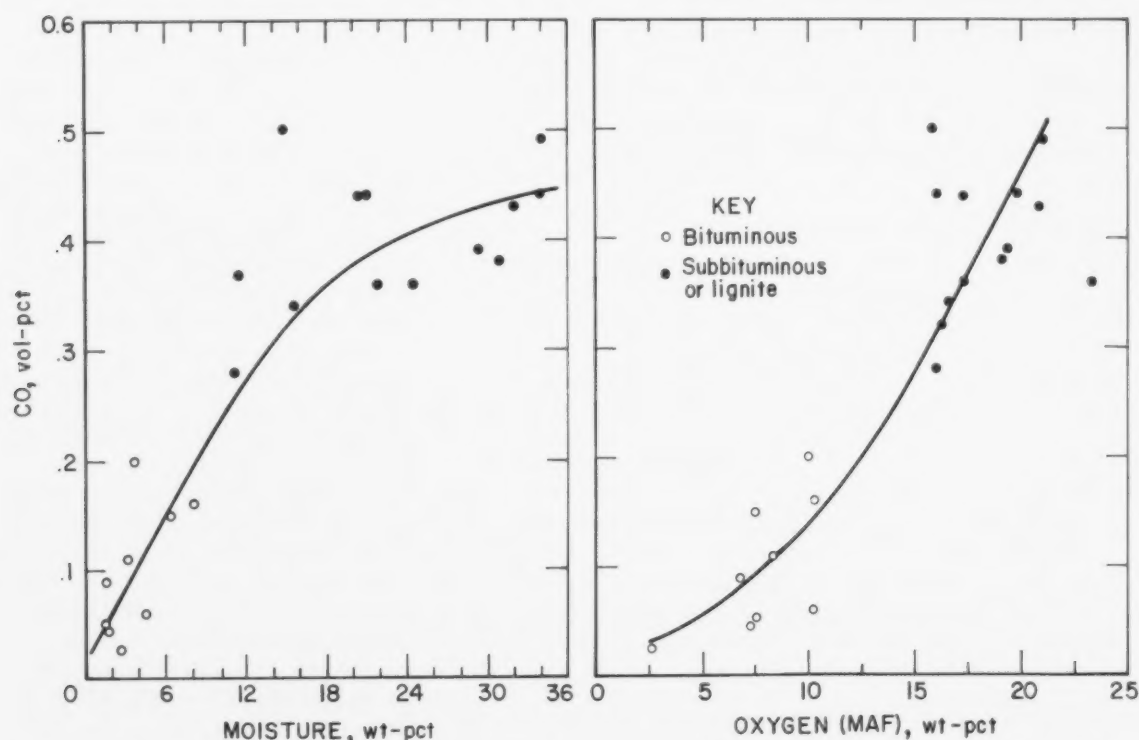


FIGURE 3. - Variation of CO formation with moisture and oxygen (MAF) content of 10- to 20-mesh dried coals on exposure to air at 25°C.

yield was not more than 0.003 vol-pct or 0.006 cm³ per 50 g for the lignite and subbituminous coals, except for the Montana Sarpy Creek stray No. 2 sample that was 0.01 to 0.015 vol-pct. In comparison, the corresponding values for most of the bituminous coals were at least an order of magnitude greater; for undried samples, they ranged from a low of 0.001 pct for the Nova Scotia Prince mine sample to a high of 14.8 pct for the Illinois Sahara No. 20 sample. The CH₄ content of coals depends greatly upon the depth and friability of the coal seam. The present results indicate that the lignite, subbituminous, and Prince bituminous coals were highly friable and/or their seams were readily degassed because of widespread fissuring or proximity to the surface. Recent core sample data by McCulloch (20) showed that the total gas content at a seam depth of about 240 m is 1 to 2 cm³ per g for the Illinois Inland coalbed, 4 to 6.5 cm³ per g for the Pittsburgh coalbed and at least 9 cm³ per g for the West Virginia Pocahontas coalbed. According to Soviet investigators,⁹ coal seams that have a CH₄ content less than 5 cm³ per g are most likely to undergo spontaneous combustion. The data from reference 20 indicate that these criteria would be met by coal seams with a CH₄ content less than that of the Pittsburgh coalbed (for example, Bruceton). Although CH₄ is not known to be vital to the spontaneous combustion process, a low concentration in the coal should at least enhance the O₂ absorption. In any event, the hazard correlation with CH₄ content should be cause for concern in the drainage of methane from coalbeds. This recently developed method for controlling and conserving the methane emission in a mine might lead to an increase in the spontaneous combustion hazard.

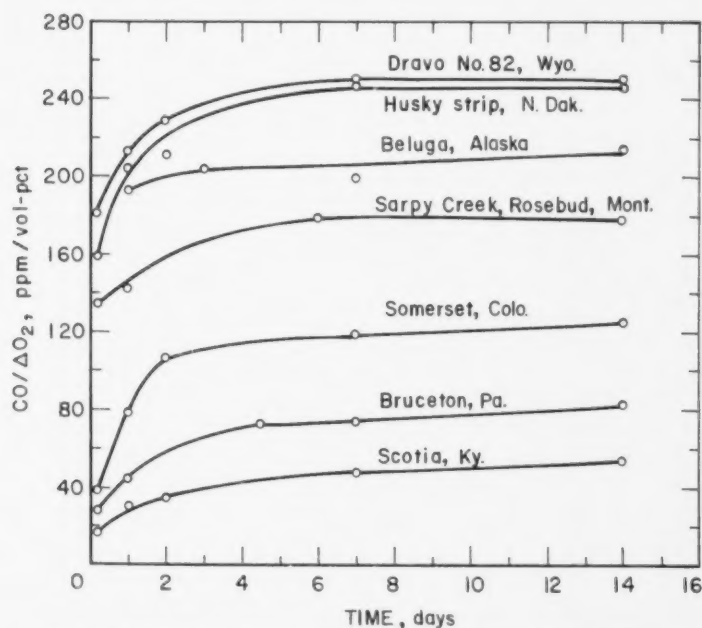


FIGURE 4. - CO/ΔO₂ ratio versus time in closed vessel experiments with 10- to 20-mesh dried coals exposed to air at 25° C.

CO/ΔO₂ Ratio

Since, in practice, the CO concentration will vary with the air ventilation rate, the CO/ΔO₂ ratio should be a more useful quantity for mining applications. In the closed vessel experiments, this CO index reached a relatively constant value even while CO and ΔO₂ were continuing to increase. Figure 4 shows typical results obtained as a function of time for dried coals of different rank; note that the CO index rises more rapidly with decreased rank and is greatest for the lower rank coals. Although the data in table 4 are not complete for all coals, it is apparent that the CO index is noticeably greater for the dried coals. The CO/CO₂ ratios were also

⁹Work cited in reference 31.

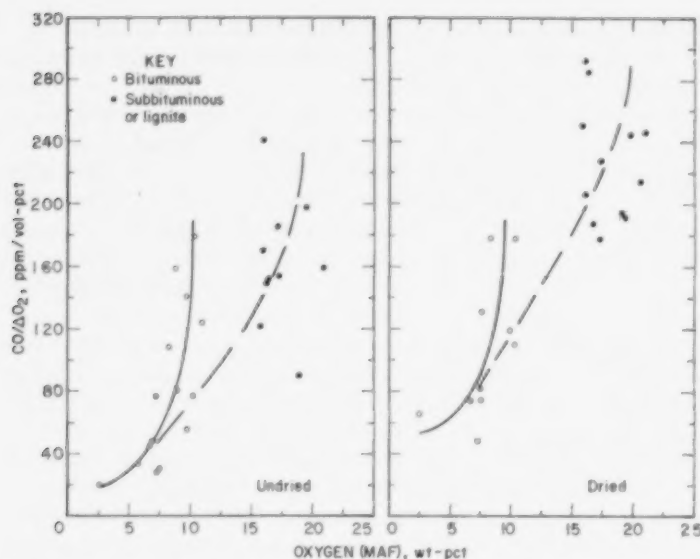


FIGURE 5. - Variation of $\text{CO}/\Delta\text{O}_2$ ratio with oxygen (MAF) content of 10- to 20-mesh dried and undried coals on exposure to air at 25°C in closed vessel experiments.

greater for dried samples. Where small differences of O_2 cannot be measured with sufficient precision, the CO/CO_2 ratios can be more meaningful as a criterion of spontaneous combustion.

The variation of CO index with rank was complicated because the CO emission did not vary consistently with the initial O_2 content of the various coals. Figure 5 compares the oxygen effect on the CO index (ppm $\text{CO}/\Delta\text{O}_2$ vol-pct) for dried and undried coal samples. The index varied with moisture content in roughly the same way. Although fair correlations were obtained with the oxygen (MAF) content of the bituminous coals,

the same correlations could not be simply extended to the subbituminous or lignite coals because of the data scatter. Nevertheless, according to the data for dried samples, a CO index greater than 180 ppm/vol-pct O_2 appears to be characteristic of coals most susceptible to spontaneous combustion, that is, lignite and subbituminous. For undried samples, the discriminating value is uncertain because of the data scatter due to any moisture effect. It is also worth noting in table 4 that the bituminous coals with a CO index between 100 and 180 included the Nova Scotia Prince coal and four western coals (Inland, Ill., Sunnyside, Utah, Somerset, Colo., and York Canyon, N. Mex.) Therefore, these coals should be suspected of having an intermediate susceptibility to self-heating and of being more hazardous than the other bituminous coals.

With increased coal temperature, the CO formation and the CO index can be expected to increase. This is shown in figure 6 from earlier Bureau studies in which the variation of the $\text{CO}/\Delta\text{O}_2$ and CO/CO_2 ratio was determined under isothermal flow conditions for the Bruceton, Pocahontas, and Somerset 10- to 20-mesh bituminous coals. The $\text{CO}/\Delta\text{O}_2$ ratios for these coals roughly doubled for each 50° increment between 50° and 150°C ; the CO/CO_2 ratios tend to be about 1 order of magnitude greater under these conditions. Such data are useful in predicting the temperature of a reacting coal. For example, a $\text{CO}/\Delta\text{O}_2$ ratio of 200 to 300 ppm/vol-pct indicates a temperature of 100°C for coals of this rank; H_2 and C_2H_4 also become detectable at about this temperature. Chamberlain (6) reported a CO index of 70 ppm/vol-pct as indicative of elevated temperature for a number of British coals.

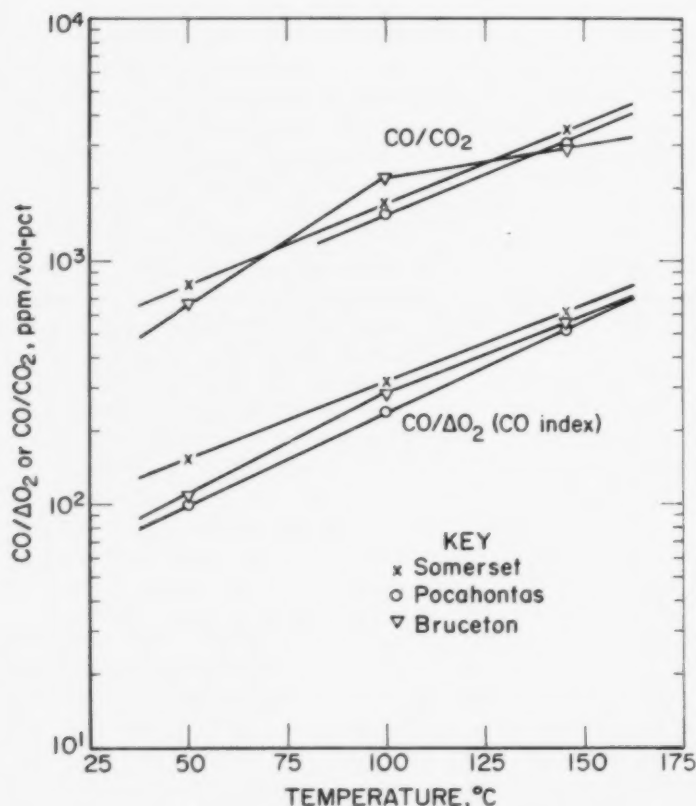


FIGURE 6. - Variation of $\text{CO}/\Delta\text{O}_2$ and CO/CO_2 ratios with temperature in $15 \text{ cm}^3/\text{min}$ flow tests with 3 undried coals of 10 to 20 mesh.

Comparison With Mine Atmosphere Analyses

The CO index ($\text{CO}/\Delta\text{O}_2$) was initially considered to be the optimum criterion for incipient combustion for the reasons suggested above; namely, that it is unaffected by duration of exposure of the coal (fig. 4), it is unaffected by dilution of the products with air, it increases dramatically with temperature (fig. 6), and it correlates well with the known susceptibilities of coals to spontaneous combustion. It was anticipated that mine atmospheres could be analyzed for CO and for O_2 deficiency and values of CO index could be derived that would resemble the values in table 4.

However, it was recognized that the constant-volume test method, as described, could introduce systematic differences from measurements of a mine atmosphere that is essen-

tially at constant pressure. Consider the definition

$$\text{CO index} = \frac{\text{final CO} - \text{initial CO}}{\text{initial O}_2 - \text{final O}_2} \quad (3)$$

During exposure of the coal to air in the closed vessel experiments, the pressure in the vessel is reduced to about $\frac{1}{2}$ atmosphere because of O_2 removal by the coal and because of repeated sampling of the air for gas analysis. In the above definition, the terms "initial CO" and "final oxygen" are approximately zero. However, the term "final CO" is a concentration at $\frac{1}{2}$ atmosphere while the term "initial O_2 " is a concentration at 1 atmosphere. Thus, the CO indices derived from the concentration values are actually twice the true ratio of CO produced to oxygen removed. From this, it would be expected that an experiment at constant pressure would give about half the value of CO index derived from constant-volume experiments.

This point was apparently borne out by the Bureau's earliest access to in-mine gas concentrations. Carbon monoxide indices were measured for 18 eastern coals, ranging from 24 to 52 ppm/vol-pct and averaging 39 ppm/vol-pct. One particular coal sample had been measured several times, giving an average CO index in the laboratory of 46 ppm/vol-pct. In the Powhatan No. 3, (Ohio) mine, where this coal sample originated, 123 air samples from 13 locations gave $\text{CO}/\Delta\text{O}_2$ averaging 19.5 ppm/vol-pct. To the extent that 19.5 is clearly less than half 46 ppm/vol-pct, it could be argued that the mine was somewhat cooler than the laboratory, which would affect the CO index in the appropriate direction.

This rationalization was negated by the in-mine experience at Somerset, Colo.,¹⁰ where the laboratory-measured CO indices for Somerset coal were consistently in the 100 to 200 ppm/vol-pct range, as shown in figures 4 and 6 and in table 4. But in the intake air to a working section of the mine, the measured CO index was 12 ppm/vol-pct. Also, there were sealed gob areas within which the oxygen concentration was effectively zero and the CO concentration held tenaciously at about 30 ppm (a CO index of 1.5 ppm/vol-pct). Only one of the sealed areas appeared to be characterized by high CO concentrations, most between 500 and 1,500 ppm, and CO indices comparable to those found in the laboratory (100 to 200 ppm/vol-pct).

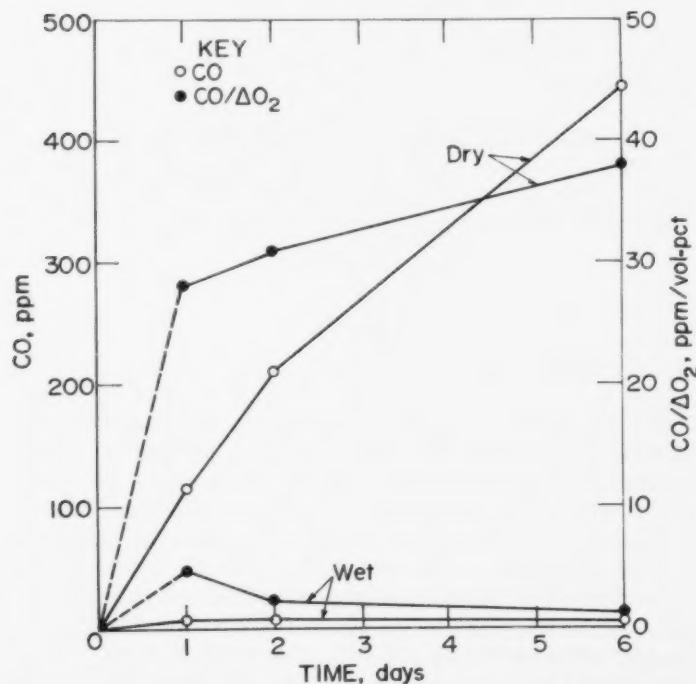


FIGURE 7. - Variation of CO and $\text{CO}/\Delta\text{O}_2$ with time for dry and wet as-mined <6.35 -mm Bruceton coal on exposure to air at 25°C in closed vessel experiments.

There is a loss mechanism for CO in mines that is not indicated by any of the laboratory work above. Also, because of the very large oxygen deficiency of most of the gob atmospheres at Somerset, even a small leakage into the active areas could cause dramatic reductions in the CO index of the working section.

Concerning the loss mechanism for CO, no progress can be reported in understanding it, but there is considerable circumstantial evidence that wetness of the coal is involved. Figure 7 shows that wet "as-mined" <6.35 -mm Bruceton coal provides almost no measurable CO and a CO index that is correspondingly low; these data are from closed vessel experiments with 50-g

¹⁰Work cited in reference 2.

coal samples. Also, in an experiment with 205 kg of wet "as-mined" <6.35-cm Bruceton coal in a 6.1-m³ closed chamber, 700 ppm CO was added to the chamber atmosphere and disappeared within 4 to 5 days (fig. 8). The CO emission would be expected to be less for wet coal than dry coal since added moisture should tend to fill or seal the micropores of the coal and, thereby retard the gas desorptions. However, no explanation is apparent for the disappearance of CO that has been observed with wet coal.

Finally, gas analyses from boreholes extending into the sealed Scotia (Ky.) mine following the explosions in 1976 were obtained. A careful review of all gas concentrations is in preparation, but for present purposes it suffices that CO from the explosion disappeared within a few weeks at each of the five borehole locations in the sealed mine.

The implication in CO monitoring is that no sophisticated interpretation should be attempted as yet of gas concentrations in gob areas (of course, a sudden upturn of CO concentration from a previously established level is always a warning of trouble). Monitoring of CO in working areas is largely unaffected by these considerations, but it is still advisable to collect the gas sample for analysis as close as possible to the incipient combustion. For this reason, the Bureau strongly recommends the tube bundle sampling method as opposed to monitoring a ventilating airstream at great distance from the source of combustion products.

O₂ Absorption Rate

The rate of O₂ consumption is proposed by some investigators as a more reliable measure of spontaneous combustion of coal than CO formation or the CO index. If the reaction is first order, the O₂ in contact with the coal should vary as an exponential function of time according to the following expressions:

$$c = c_0 e^{-kt}, \quad (4)$$

$$\ln c = -kt + \ln c_0, \quad (5)$$

where c refers to O₂ concentration at time t , c_0 is initial O₂ concentration, and k is a constant that varies with the physical and chemical nature of the coal sample. In the present desorption experiments, the O₂ reduction in the reaction vessel was not consistent with the above expressions over the entire period of desorption; figure 9 shows a semilog plot of the O₂ partial pressure with time for dried samples of several coals. Essentially, the O₂ concentration decreased exponentially with time for about 24 hours, after which the reaction changed to a lower rate, as evidenced by a change in slope of the curves in figure 9. Generally, the deceleration of the absorption rate tended to be greatest for the most reactive coals, such as the Gascoyne strip and Beluga lignite samples. The change in reactivity for each coal is not surprising since the total pressure varied (decreased) significantly with time in these constant-volume experiments. Under constant pressure conditions, the O₂ absorption would not be limited by any total pressure effect, and the relationship of $\ln P_{O_2}$ with time would be expected to be linear for extended time periods until the O₂ concentration became a limiting factor.

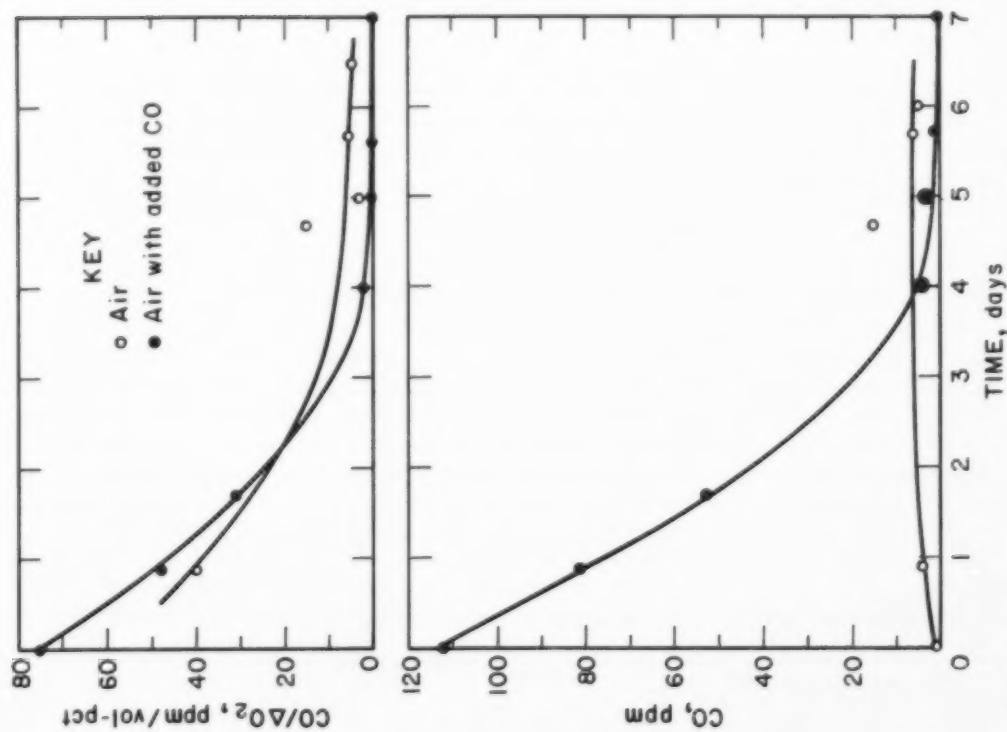


FIGURE 8. - Variation of CO and CO/ΔO₂ with time for wet "as mined" 6.35-cm Bruceton coal with and without the addition of CO in large-scale experiments (205 kg coal in 6.1 m³ closed chamber).

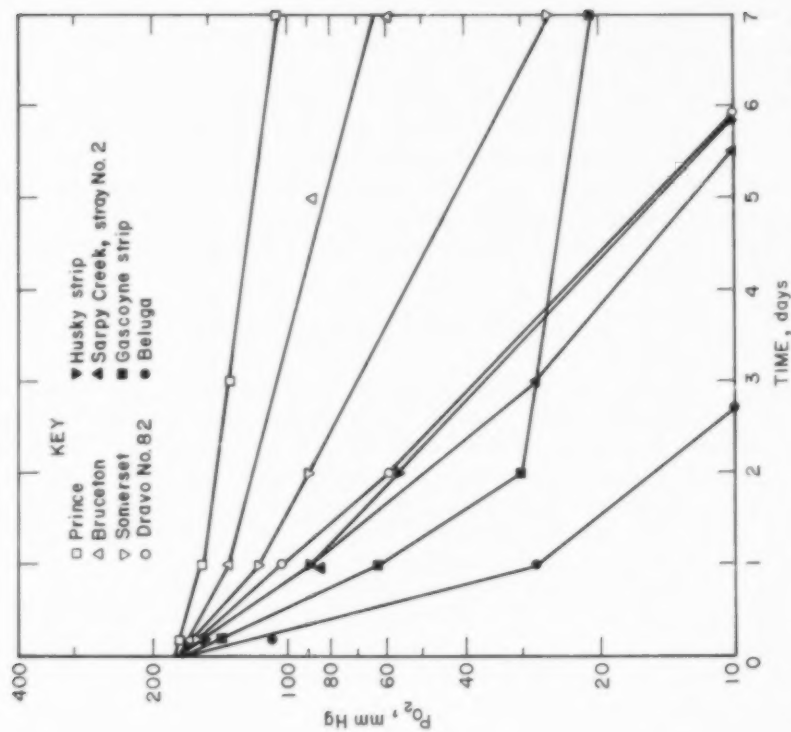


FIGURE 9. - Semilog plot of oxygen partial pressure (P_{O₂}) with time for 10- to 20-mesh dried coals exposed to air at 25° C in closed vessel experiments.

Because of the total pressure variation in the desorption experiments, the initial O_2 absorption rates are considered to be the most meaningful way of predicting relative reactivity for each coal. For the dried samples of 10- to 20-mesh crushed coal, the average rates for the initial 24-hour sorption period ranged between 0.1 and 0.8 cm^3/hr (0.002 and 0.016 $cm^3/hr-g$ of coal) for the bituminous coals and between 0.8 and 1.4 cm^3/hr (0.016 and 0.028 $cm^3/hr-g$ of coal) for most of the subbituminous and lignite coals. As shown in figure 10 these initial rates varied in direct proportion to the oxygen content of the coal. Regression analysis gave the following expression for these data:

$$dO_2/dt = 0.062(O)_{coal} - 0.055, \quad (6)$$

where dO_2/dt is in cubic centimeters per hour and $(O)_{coal}$ is in weight-percent (MAF). Thus, the coals most susceptible to spontaneous combustion appear to have an O_2 absorption rate of at least 0.016 $cm^3/hr-g$ (~ 0.02 $mg/hr-g$) when the coals are dry and finely divided. In the case of undried coal samples, the rates tended to be lower than those shown in figure 10. However, similar data obtained by other Bureau investigators (24) indicate that the maximum O_2 absorption rate for some coals can occur at intermediate levels of moisture content; their values ranged between 0.03 and 0.09 $mg/hr-g$ for a coarse-sized North Dakota lignite at 25° C and moisture contents between 5.0 and 32.8 wt-pct. These investigators also found the absorption reaction to be first order with respect to the O_2 partial pressure for reaction times of up to a few hours. In the present experiments, the rate dependency upon O_2 concentration of the atmosphere was somewhat greater, probably because of coal composition and particle size differences, and decreased after extended periods of oxidation (>24 hours).

Soviet investigators claim that the O_2 absorption rate is not always a reliable criterion of spontaneous combustion. In the comprehensive report by Veselovskii,¹¹ the absorption rates of coals in laboratory tests were described by the following expression:

$$dO_2/dt = k' P_{O_2}, \quad (7)$$

where P_{O_2} is the oxygen partial pressure of the atmosphere and k' is the reactivity constant of the coal as determined from its average O_2 absorption rate ($cm^3/hr-g$) during a fixed period of exposure. However, these rates can display a complex dependence upon the extent of pulverization and the amount of CH_4 desorbed. The residual CH_4 content of the coal was reported to be the best indicator for predicting a spontaneous combustion hazard in a mine. For example, (32) coal seams that were known to produce spontaneous heating and O_2 absorption rates (24 hours) between 0.009 to 0.091 $cm^3/hr-g$ and a CH_4 content less than 5 m^3 per ton of coal (5 cm^3/g); seams that did not produce such endogeneous fires had O_2 absorption rates between 0.015 and 0.072 $cm^3/hr-g$ and a CH_4 content greater than 5 m^3 per ton. If indeed a methane content of less than 5 m^3 per ton is critical as a criterion of spontaneous combustion susceptibility, the

¹¹Work cited in reference 31.

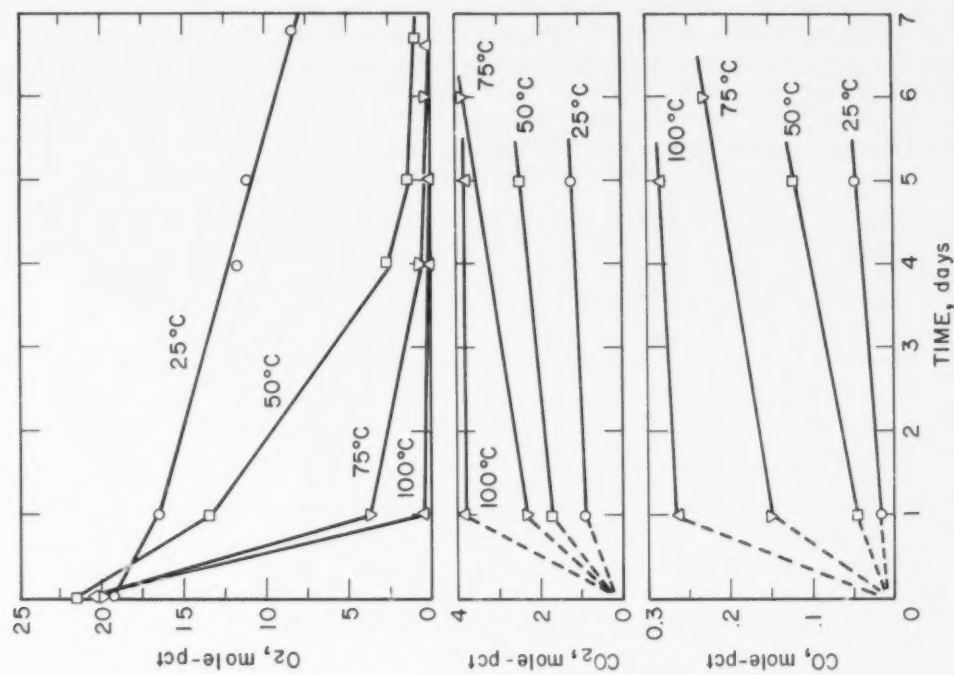


FIGURE 11. - Gas chromatographic analysis of CO , CO_2 , and O_2 versus time in closed vessel experiments with 10- to 20-mesh undried Bruceton coal exposed to $18O_2$ simulated air at 25°, 50°, 75°, and 100° C.

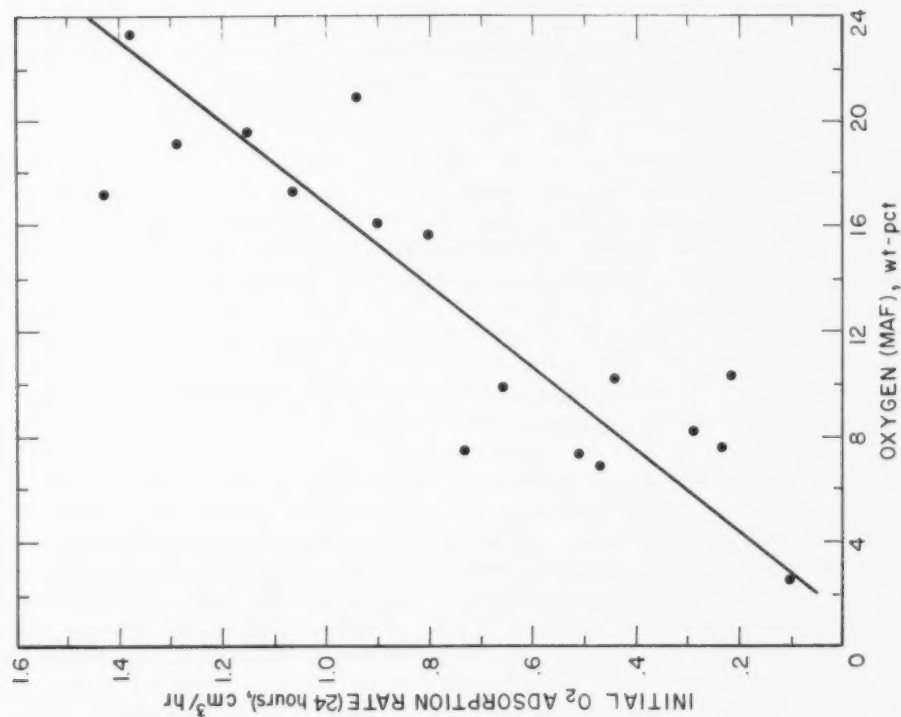


FIGURE 10. - Variation of initial O_2 absorption rate (24 hours) with oxygen (MAF) content of 10- to 20-mesh dried coals exposed to air at 25° C in closed vessel experiments.

coals meeting this criterion should generally have relatively high O_2 absorption rates. To establish the reliability of this criterion, data are needed on the effect of varying methane content on the spontaneous combustion tendency of the given coal.

Exposure of Coals to $^{18}O_2$ -Argon Atmosphere

The closed vessel tests in which air was replaced with 79 pct argon and the 21 pct $^{18}O_2$ isotope were made with only a few bituminous coals, including the Bruceton and Somerset mine coals. Total concentrations of the gaseous products were determined by gas chromatography and their isotopic distributions by mass spectrometry. Figure 11 shows the total O_2 , CO, and CO_2 histories that were obtained with 10- to 20-mesh samples of the undried Bruceton coal for 1 week exposures at 25°, 50°, 75°, and 100° C; the sample loading was 25 g in the 110-ml reaction vessel (0.23 g/cm³). Consistent with tests in normal air (21 pct $^{16}O_2$), the total CO or CO_2 formation increased with increasing time and temperature and became limited by the diminishing oxygen in the vessel. Thus, the CO and CO_2 concentrations at 100° C were near maximum within 1 day since the O_2 had decreased to less than 1 pct. With decreasing temperature, the rate of O_2 reduction and its effect on the gas emissions tends to be progressively less critical. The CO_2 levels were between 1 and 2 orders of magnitude greater than the CO levels but still substantially less than expected for the amounts of O_2 depletion. An analysis of the isotopic product distributions was necessary to provide a possible explanation for these results.

Mass spectrometric analyses of the desorption or oxidation products indicated that little apparent reaction occurred between the coals and the $^{18}O_2$ isotope at 25° C (table 5). Reaction of the coals with this isotope could conceivably yield such ^{18}O containing compounds as $C^{18}O$, $C^{18}O_2$, and $C^{16}O^{18}O$ whose concentrations should vary with the exposure period. The $C^{16}O^{18}O$ product was possible because $^{16}O^{18}O$ was an impurity (<5 pct) in the $^{18}O_2$ reactant and also because free or combined $^{16}O_2$ was initially present in the coals. However, although such carbon oxide isotopes were detected at 25° C, their combined concentrations were a small fraction of the total carbon oxides and they varied little with exposure times of up to 1 week. Figure 12 shows the $C^{18}O$, $C^{18}O_2$, and $C^{16}O^{18}O$ analytical data obtained for the Bruceton coal at 25° and 50° C. Even at 50° C, the only convincing evidence of any $^{18}O_2$ reaction was the formation of $C^{16}O^{18}O$ which increased with exposure time and was two to four times greater than that detected at 25° C.

The effect of increasing temperature is more clearly evident in figure 13 where the isotopic product distributions are compared after 24-hour exposures of the coals at 25° to 100° C. This exposure time was selected because of the rapid oxygen consumption at the higher temperatures. Essentially, these data show that the $C^{18}O$ and both $C^{16}O_2$ and $C^{16}O^{18}O$ increase noticeably when the temperature is increased above 50° C or 75° C, whereas the $C^{18}O_2$ decreases sharply above 50° C; $C^{16}O$ data are not shown because of their incompleteness in this test series. The negative temperature coefficient for the $C^{18}O_2$ species is offered without explanation. Nevertheless, it is apparent that the formation of $C^{16}O^{18}O$ is a better criterion of reaction than $C^{18}O$ or $C^{18}O_2$.

for coals exposed to $^{18}\text{O}_2$. Similar results were obtained with a western bituminous coal (Somerset²) that normally tends to yield more CO than the eastern bituminous coals (table 4). These results are summarized in table 5. Generally, the formation of ^{18}O -containing products increased with decreasing coal particle size, indicating the reactions with the $^{18}\text{O}_2$ isotope were heterogeneous and surface controlled.

TABLE 5. - Mass spectrometric analyses from desorption experiments with Bruceton and Somerset coals exposed to $^{18}\text{O}_2$ -argon atmosphere at various temperatures

(Exposure time--24 hours; sample loading--25 or 3.7 g in 110 ml-vessel)

Coal ¹	Sample, g	Analyses, mole-pct							
		¹⁸ O ₂	CO ²	C ¹⁸ O	C ¹⁶ O	² CO ₂	C ¹⁸ O ¹⁸ O	C ¹⁶ O ¹⁶ O	C ¹⁶ O ¹⁸ O
25° C									
Bruceton	~25	16.5	0.02	0.037	ND	0.86	0.025	0.92	0.044
Somerset	~25	>8.0	<.14	.070	0.060	ND	.060	.07	.060
Do...	3.7	>8.0	ND	.095	.050	ND	.090	.06	.090
50° C									
Bruceton	~25	13.5	0.05	0.033	ND	1.75	0.025	1.53	0.077
Somerset	~25	0.01	.16	.026	0.166	.84	<.125	.65	.050
		>6.8	ND	.140	.260		.160	.51	.110
75° C									
Bruceton	~25	3.01	0.15	0.053	ND	2.32	0.006	1.93	0.096
Somerset	~25	.35	.76	.094	1.037	ND	.014	3.91	.106
Do...	3.7	.79	ND	.140	.270	ND	.090	.88	.230
100° C									
Bruceton	~25	0.27	0.26	0.081	ND	3.84	<0.001	4.17	0.300
Somerset	~25	<.01	.68	.054	1.738	8.60	<.005	5.89	.117
		.05	ND	.085	1.360	ND	<.005	6.11	.220
Do...	3.7	.05	ND	.190	.840	ND	.050	1.88	.580

ND Not determined.

¹~25-g sample with 10- to 20-mesh coals and 3.7-g sample with 100- to 200-mesh coals.

²Gas chromatographic analyses.

These data provided some insight to the fate of the O_2 reactant and the possible mechanisms of reaction in such exposures of crushed coals. The C^{16}O and C^{16}O_2 were the main gaseous products instead of C^{18}O and C^{18}O_2 and indicated that most of the $^{18}\text{O}_2$ consumption was not attributable to oxidation processes. Essentially this implies that the primary low temperature reactions involved mostly absorption of $^{18}\text{O}_2$. The desorption of the free or loosely combined carbon oxides present in the coal, namely C^{16}O (decarbonylation) and C^{16}O_2 (decarboxylation), from previously absorbed $^{16}\text{O}_2$ accounted for most of the oxidation products. The chemisorption of oxygen on carbon surfaces and the formation of carbon-oxygen surface complexes has been well demonstrated (12, 18). If each carbon surface site of the coal is designated C_s , the sorption of $^{18}\text{O}_2$ onto an unoccupied site can be expressed as follows:

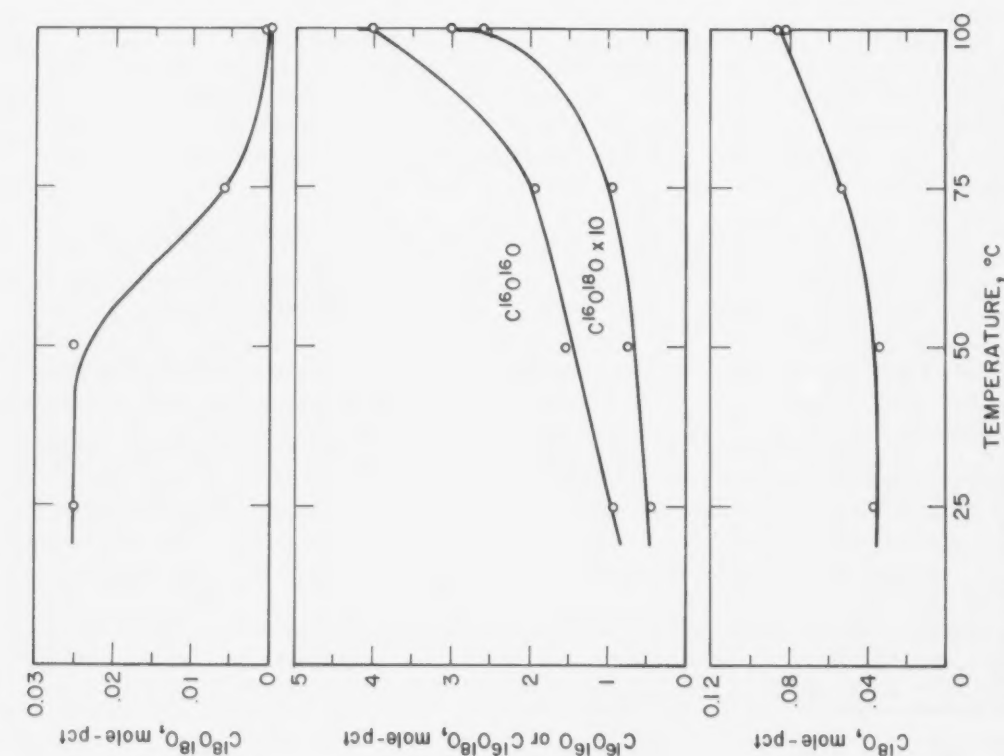


FIGURE 13. - Temperature effect on formation of carbon oxide isotopes in $^{18}\text{O}_2$ desorption experiments with 10- to 20-mesh Bruceton coal.

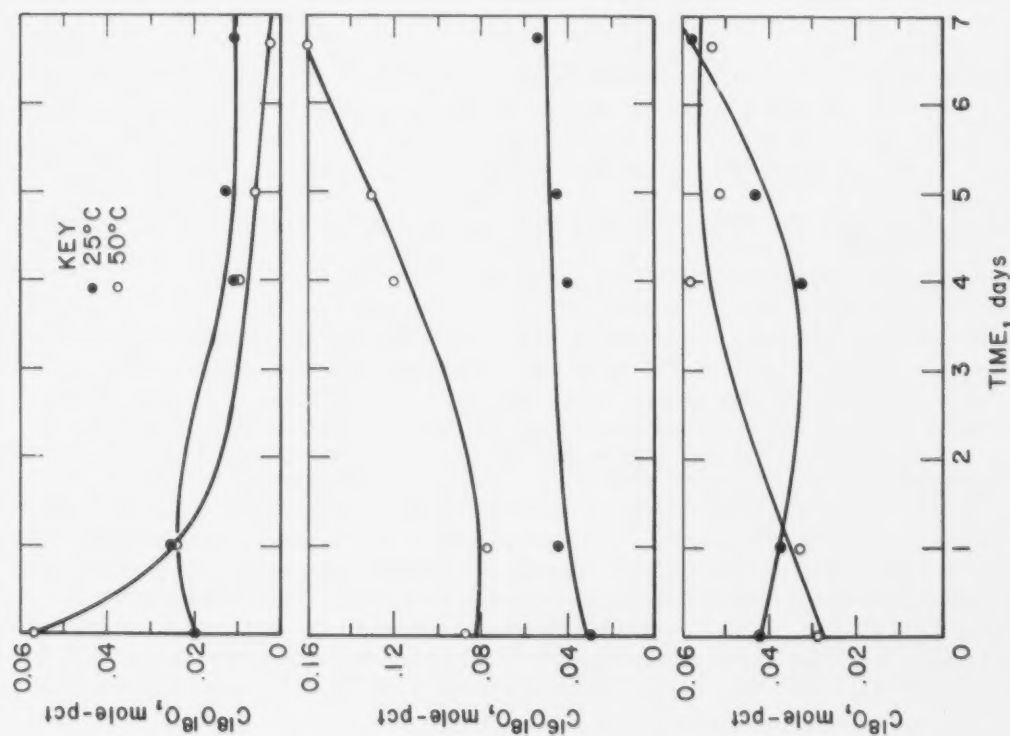
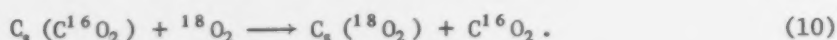
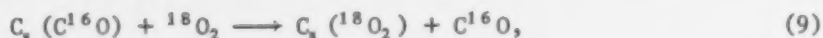


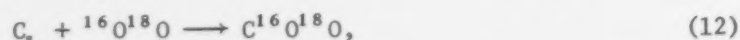
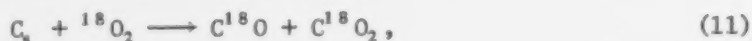
FIGURE 12. - Mass spectrometric analyses of C^{18}O , $\text{C}^{16}\text{O}^{18}\text{O}$, and $\text{C}^{16}\text{O}^{18}\text{O}_2$ versus time in closed vessel experiments with 10- to 20-mesh undried Bruceton coal exposed to $^{18}\text{O}_2$ simulated air at 25° and 50°C .



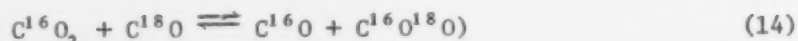
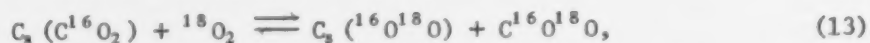
where $C_s({}^{18}O_2)$ represents a carbon-oxygen surface complex in which the oxygen is loosely bonded. For the case of occupied surface sites, simultaneous sorption and desorption would be expected so that the following expressions would depict the displacement of the $C^{16}O$ and $C^{16}O_2$ initially in the coal:



Thus, $C^{16}O$ and $C^{16}O_2$ could form by simple molecular exchange, whereas the formation of other gaseous products ($C^{18}O$, $C^{18}O_2$, and $C^{16}O^{18}O$) requires the assumption of oxidation, such as



or the assumption of isotopic oxygen exchange, such as



where $C^{16}O^{18}O$ is more likely to form than $C^{18}O$ or $C^{18}O_2$, as in the present experiments. Although such exchange reactions have been shown to be possible by other investigators, the chemical kinetics are controversial and have been mostly studied at rather high temperatures (22, 30). In any event, both oxidation and isotopic exchange reactions were relatively unimportant in this work up to at least 50° C. Also, since the total concentrations of carbon oxide emissions could hardly account for the ${}^{18}O_2$ depletion, most of the ${}^{18}O_2$ apparently ended up physically or chemically bonded to unoccupied coal surface sites, as proposed by equation 8.

It may be argued that any low temperature oxidation by ${}^{18}O_2$ could not be detected because of the small mass concentrations of ${}^{18}O_2$ and ${}^{18}O$ containing carbon oxide products compared to the much higher mass concentrations of ${}^{16}O_2$ and ${}^{16}O$ carbon oxides that were present in the coal from previous exposure. However, if oxidation did occur at 25° C, at least some small but significant increases in the ${}^{18}O$ -containing products should have resulted with increasing exposure time. As noted in figure 12, only the 50° data (particularly $C^{16}O^{18}O$) show such a trend.

Based on these data, small concentrations of CO or CO₂ in a coal mine entry cannot always be considered as evidence of ongoing oxidation or an incipient stage of combustion. For bituminous coals, the data suggest that the emission of these gases at temperatures up to at least 50° C largely represent decarbonylation or decarboxylation products from previous reactions by the coals in their virgin state; the reactions could have extended back to the coalification stage of the coalbed. For subbituminous and lignite coals,

the corresponding critical temperatures would be expected to be less than 50° C because of their greater reactivity; this is confirmed by the self-heating data given in the following section of this report. These data point to the importance of establishing the normal background CO and CO₂ concentrations in the different working areas of a mine.

Self-heating of Coals

The self-heating tendency of a coal mass can vary with its porosity, moisture content, and ventilation rate and with the humidity of the ventilating air. Exploratory experiments in this work indicated that self-heating of most coals could be obtained with a maximum particle size of about 50 to 70 mesh at an air flow of about 50 cm³/min; here, the air flowed around the coal sample and therefore, the flow within the coal bed was substantially lower than the reported rate. Moisture or humidity effects appeared to be greatest for the lowest rank coals.

Initial data were obtained with undried samples of the bituminous-grade coals in dry air. These coals required an ambient temperature of at least 60° C to achieve a sustaining self-heating reaction. Figure 14 shows the temperature histories obtained for 50- to 70-mesh samples of the Somerset bituminous coal that was exposed to dry air at various initial temperatures.

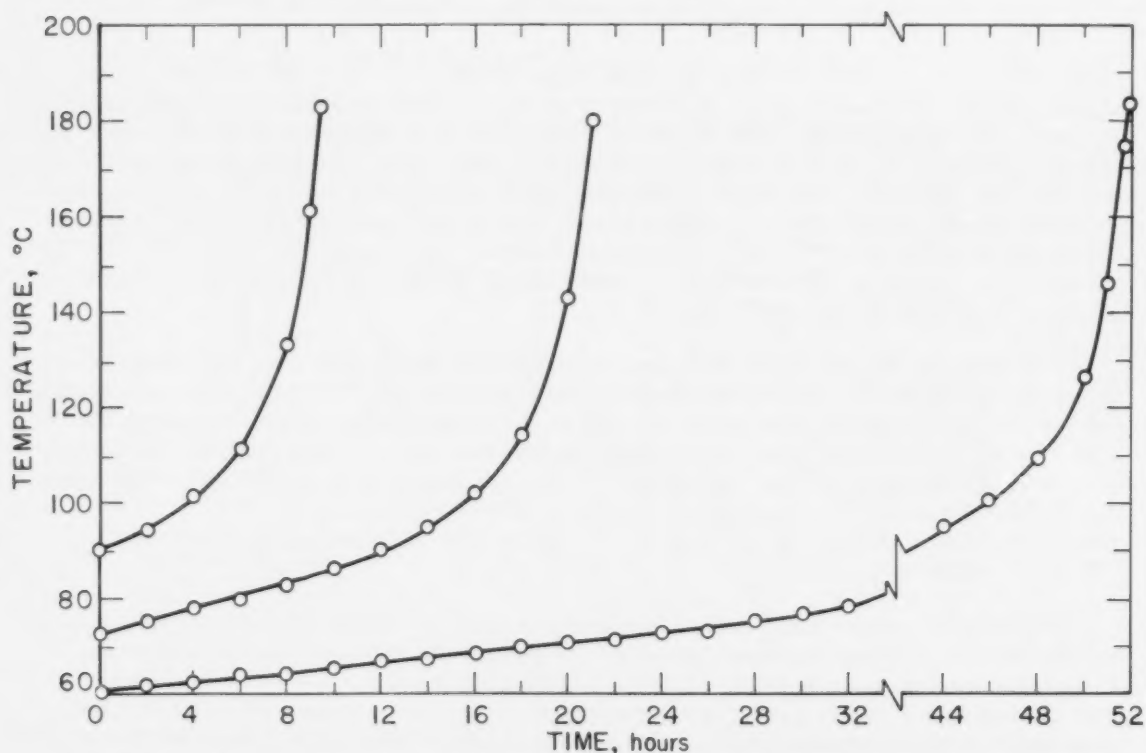


FIGURE 14. - Temperature histories in self-heating experiments with 50- to 70-mesh undried Somerset coal in dry air at 60°, 70°, and 90° C initial temperatures.

Actual duration of each experiment was at least 2 hours longer than shown since the initial heat-up period in flowing nitrogen is not included here. As noted, this coal self-heated within 10 hours at 90° C but required an exposure time of over 50 hours at 60° C before the reaction became highly exothermic; below 60° C a sustained exothermic reaction was not observed even with a much finer size coal of 100 to 200 mesh. Generally, the initial rate of temperature rise increased with increasing temperature and decreasing coal rank. For the Somerset coal, the initial rate of temperature rise increased from about $\frac{1}{2}$ ° per hour to over 2° per hour when the initial temperature was increased from 60° to 90° C. Although the experiments were terminated before ignition became manifest, it can be assumed that the ignition temperature of the given coal would have been eventually reached if the reaction had been permitted to continue.

The minimum self-heating temperature of the Sahara No. 20 coal was also approximately 60° C in dry air, whereas the other bituminous coals required temperatures between 70° and 105° C. Figure 15 compares the temperature histories that were obtained for several of the high-rank coals at or near their self-heating temperatures. For these coals, a reduction in particle size (50 to 70 mesh versus 100 to 200 mesh) or the use of saturated moist air

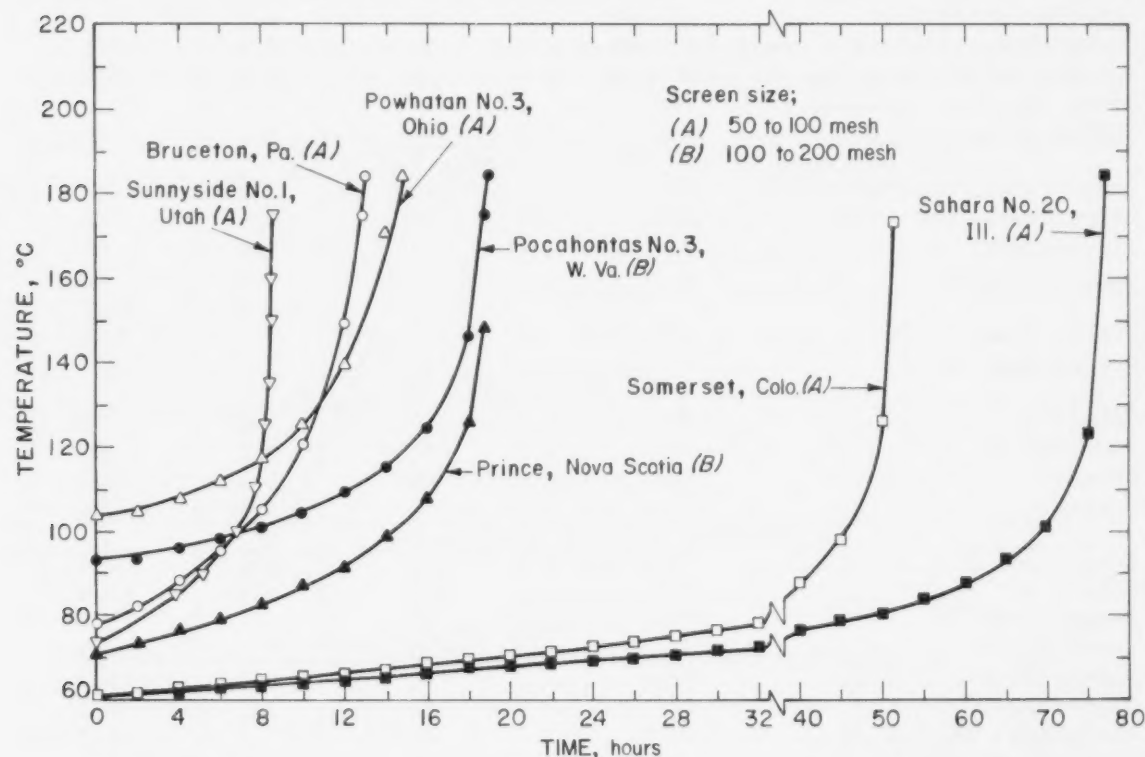


FIGURE 15. - Temperature histories in self-heating experiments with various undried bituminous coals in dry air and one (Prince) in moist air. Particle size is given in table 6.

instead of dry air usually increased their reactivity; however, these effects tended to be less noticeable with increasing temperature and were not pronounced at the self-heating temperature of these high-rank coals. Coal volatility also had a relatively small effect. For example, the lowest self-heating temperature was approximately 80° C for the Bruceton high volatility coal and 90° C for the Pocahontas low volatility coal. The self-heating data for the various coals examined in this work are presented in table 6. Table 6 also includes data obtained by the National Bureau of Standards for a few coals using an adiabatic heating apparatus similar in design to that of this work (10).

TABLE 6. - Summary of data from self-heating tests in adiabatic calorimeter

(Air flow--50 cm³/min)

Mine	Location	Self-heating temperature, ° C	Initial dT/dt, ° C/hr	Apparent activation energy, ΔE, kcal/mole
LIGNITE: 100 TO 200 MESH; MOIST AIR				
Beluga.....	Alaska.....	32	4.5	8.5
Gascoyne strip.....	N. Dak.....	30	5.9	5.1
Husky strip.....	N. Dak.....	30	5.0	7.1
Center strip.....	N. Dak.....	30	6.5	8.3
Darco strip.....	Tex.....	30	6.0	9.0
Sandow strip.....	Tex.....	30	3.0	ND
SUBBITUMINOUS: 100 TO 200 MESH; MOIST AIR				
Sarpy Creek, Rosebud.....	Mont.....	30	3.0	6.6
Sarpy Creek, stray No. 2.....	Mont.....	30	5.0	7.0
Jim Bridger.....	Wyo.....	32	3.8	ND
Mammoth Divide.....	Mont.....	¹ 30	1.9	ND
		70	5.0	11.2
Dravo, seam No. 80.....	Wyo.....	30	3.6	6.5
Dravo, seam No. 82.....	Wyo.....	70	5.0	12.5
BITUMINOUS: 100 TO 200 MESH; MOIST AIR				
Sahara No. 2.....	Ill.....	¹ 30	ND	ND
Somerset No. 2.....	Colo.....	¹ 30	3.0	ND
Prince.....	Nova Scotia	70	1.5	13.3
Scotia.....	Ky.....	¹ 70	1.8	ND
BITUMINOUS: ~50 TO 70 MESH; DRY AIR				
Sahara No. 20.....	Ill.....	60	0.4	15.3
Sahara No. 21.....	Ill.....	² 75	1.8	17.9
Somerset No. 1.....	Colo.....	60	.6	13.9
Sunnyhill No. 9.....	Ohio.....	² 70	3.3	17.3
Sunnyside No. 1.....	Utah.....	² 70	3.2	15.9
Bruceton.....	Pa.....	80	2.5	9.2
Pocahontas No. 3.....	W. Va.....	90	.8	16.7
Powhatan No. 3.....	Ohio.....	105	1.0	15.4

ND Not determined because of data limitations.

¹Noticeable exotherm but reaction not sustained.²Data from experiments by National Bureau of Standards; reported in reference 17.

Low-rank coals were capable of sustained self-heating at temperatures noticeably below 60°C . As noted in table 6, 100- to 200-mesh samples of all the lignites and most of the subbituminous coals self-heated at near-ambient temperature ($\sim 30^{\circ}\text{C}$). To obtain such low reaction threshold temperatures, it was necessary to use dried coal samples and saturated moist air; here, special effort was taken to minimize the intrinsic moisture content of the coal since even a few percent could affect reactivity. Figure 16 illustrates the large humidity effect that is possible with thoroughly dried samples of the Dravo Seam No. 80 subbituminous coal in air and nitrogen. Based on these data, an exotherm of at least 10°C appears possible due to the heat of moisture adsorption alone (note moist N_2 curve) and apparently is sufficient to promote self-heating of this coal in moist air. The bituminous coals also displayed this "heat-of-wetting" effect but the temperature rises were insufficient to produce a sustained reaction. This is apparent for the Bruceton and Somerset coals in figure 17 in which the temperature histories are compared for several different ranked coals that were exposed to moist air at 30°C . Other coals that were examined gave similar results, depending upon their rank. The high reactivity of the dried coals in moist air appears to be comparable to that possible in a dry oxygen atmosphere, according to Stott (25). He obtained ignition of a subbituminous coal in both saturated air and dry oxygen within the same time of exposure, 12 hours at 18°C .

Since adiabatic conditions were simulated in these experiments and the flow velocity through the coal bed was negligible, the self-heating rates of

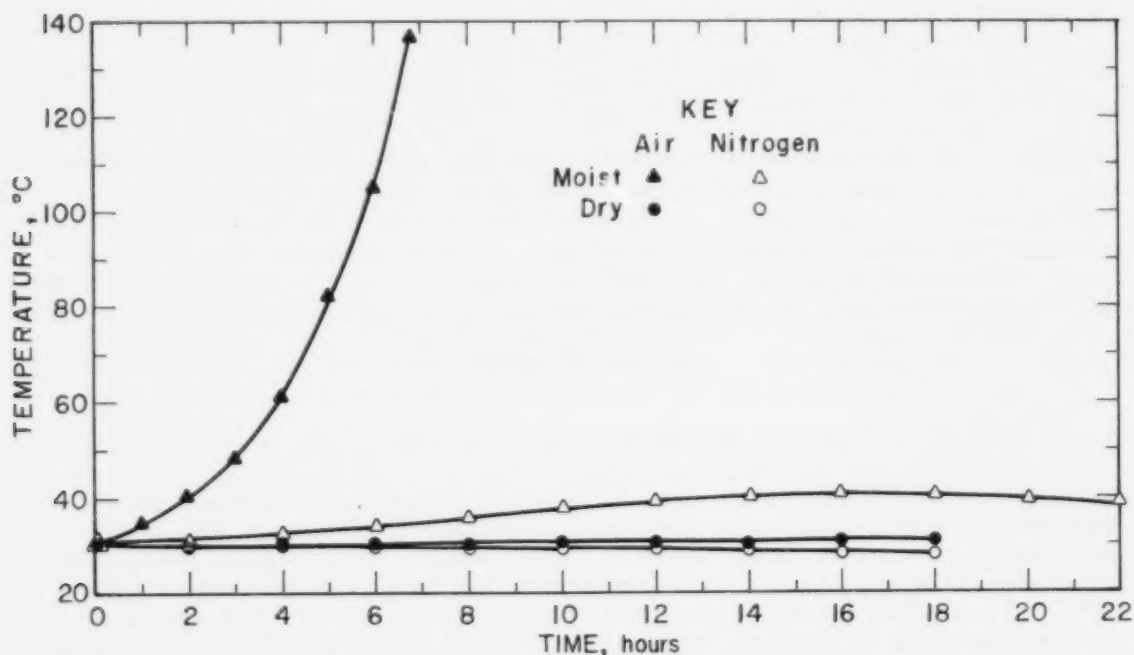


FIGURE 16. - Humidity effects in self-heating experiments with 100- to 200-mesh dried Dravo seam 80 coal in air and nitrogen atmospheres at 30°C .

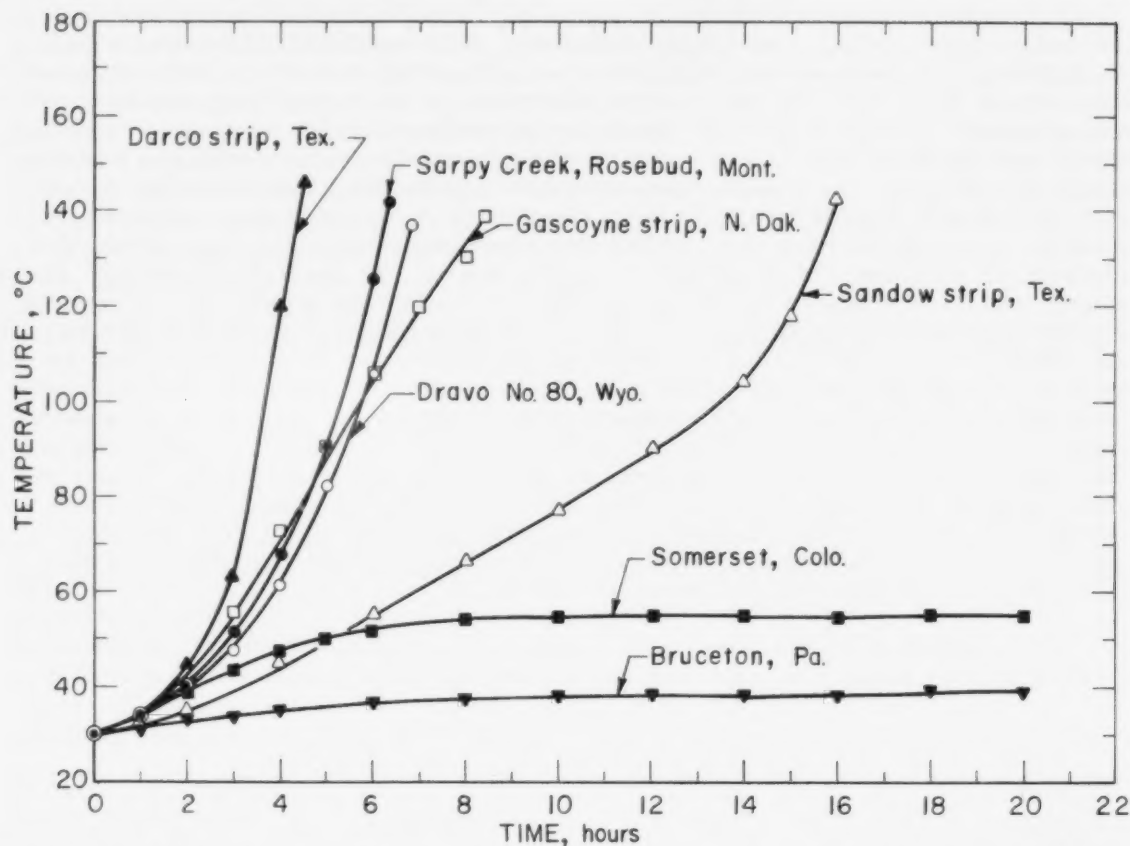


FIGURE 17. - Temperature histories in self-heating experiments with 100- to 200-mesh dried samples of low and high rank coals in moist air at 30° C.

the coals should be essentially equivalent to their chemical heat release rates. For such conditions, the self-heating equation (1) given at the outset of this report reduces to the case where heat loss (q_2) is negligible.

$$dT/dt = \frac{QZ}{c} e^{-E/RT}, \quad (15)$$

or

$$\ln dT/dt = -E/RT + \ln k, \quad (16)$$

where the rate of temperature rise (dT/dt) of the coal is an exponential function of temperature and k is equal to the rate coefficient QZ/c . The temperature rise rates from this work were largely consistent in this respect and tended to correlate for each coal over the range of experimental temperatures. Figure 18 is a semilog plot ($\log dT/dt$ versus $1/T$) of the results for the Somerset coal at initial temperatures of 60°, 70°, and 90° C. A single curve can be drawn to approximate all the rate data, although the slope tends to decrease at the higher temperatures (>140° C) where the reaction was presumably oxygen limited; the oxygen limitation would be less where the air

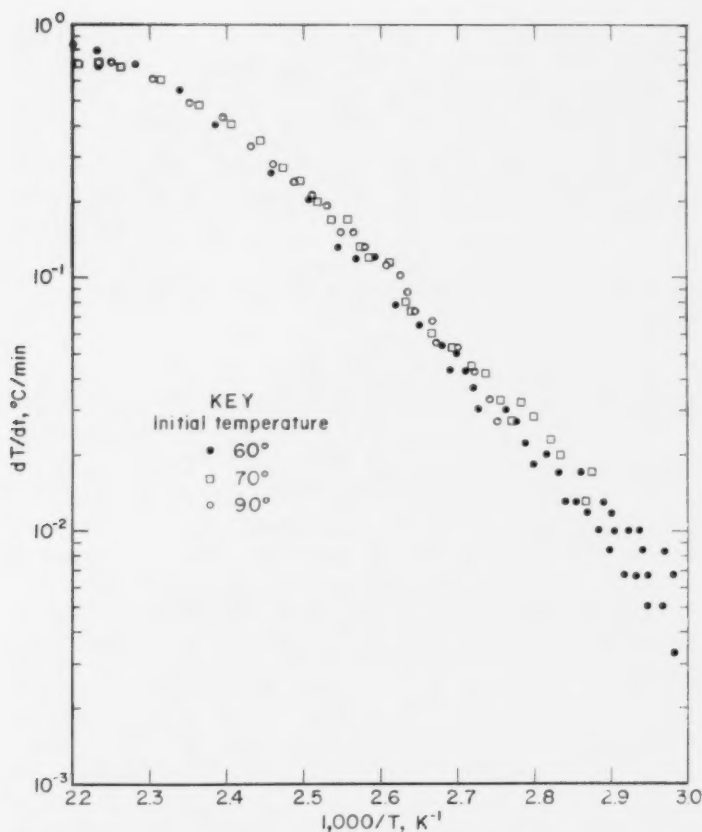


FIGURE 18. - Log dT/dt versus reciprocal temperature for self-heating experiments with 50- to 70-mesh undried Somerset coal in dry air at 60°, 70°, and 90° C initial temperatures.

were complicated by the heat-of-wetting effect and were not necessarily a monotonic function of temperature at all temperatures. The global activation energies from rate data for these coals were largely less than 10 kcal/mole, at least in the low-temperature range of ~30° to 70° C. These lower activation energies reflect the higher reactivities of lower rank coals.

The above data are roughly consistent with the findings of Soviet investigators for the early stages of coal combustion. Oreshko¹³ reported that the initial step is the chemisorption of oxygen with an activation energy of 3 to 4 kcal/mole and that this is followed by the decomposition of the chemisorbed oxygen complex with an activation energy of about 6 kcal/mole. The latter step would involve decarbonylation or decarboxylation, similar to that noted in the present ¹⁸O₂ tracer experiments. The subsequent oxidation step reportedly involves the formation of an "oxycoal" compound with an activation

passes through the coalbed instead of around it. Apparent global activation energies (ΔE) derived from the slopes ($-E/r$) of such rate plots were between 12 and 14 kcal/mole for the Somerset coal.

As shown in table 6, the global activation energies for the self-heating data of all the bituminous coals fall in the 10- to 20-kcal/mole range. They reflect reactivity of the coals above 60° C and are typical of surface oxidations in which the reaction rate is controlled by O₂ absorption, CO or CO₂ desorption, or other physical processes that are less temperature-dependent than the actual oxidation reaction. These temperature coefficients are also consistent with those obtained from the CO and CO₂ emission rates of such coals at elevated temperatures.¹² In comparison, the rate data for the lower ranked coals

¹²Work cited in reference 17.

¹³Work cited in reference 29, p. 251.

energy of the order of 16 kcal/mole, similar to that observed at elevated temperatures in this work. In reality, all of these reactions compete simultaneously but their importance will depend upon both the reactivity of the coal and the reaction temperature. Both Soviet (23) and English (4) investigators claim that 70° C is the approximate critical temperature above which the oxidation of their coals undergoes a radical change and accelerates greatly. Reznik (23) reported that the activation energy is approximately 5 kcal/mole for the low-temperature state (20° to 70° C) and 30 kcal/mole for the high-temperature stage (>70° C). The value of 5 kcal/mole appears to agree well with those obtained in this work for the low-temperature stage of reaction of the lignite and subbituminous coals.

Self-heating temperatures are substantially lower under adiabatic than nonadiabatic conditions. The latter conditions are more common in real life and include those used to define so-called minimum AIT's; these are determined in a heated vessel at a fixed temperature and involve relatively high heating rates to overcome the heat losses. Table 7 compares the two different sets of temperatures for 100- to 200-mesh samples of four different coals that were investigated. Although the minimum AIT's do not vary greatly, the differences have practical significance and reflect a greater ignition hazard for the western or lower ranked coals. This is especially important in determining the safe external surface temperature for permissible electrical equipment in coal mines, which are presently limited to 150° C by Federal Schedule 2G (28). The data in table 7 indicate that the value of 150° C may not be sufficiently conservative, particularly for the western coals; however, this assumes the coal dust layers are several centimeters thick so that heat losses are not excessive.

TABLE 7. - Comparison of adiabatic self-heating temperatures and minimum AIT's of four coals in air at atmospheric pressure

(Particle size--100 to 200 mesh)

Mine	Location	Self-heating temperature, ¹ ° C	Minimum AIT, ² ° C
Darco strip.....	Tex.....	30	120
Dravo, seam No. 82.....	Wyo.....	30	120
Somerset.....	Colo.....	60	130
Bruceton.....	Pa.....	80	140

¹100-g dried sample in adiabatic calorimeter with moist air.

²50-g undried sample in 500 cm³ open vessel with dry air.

In the application of these data, both temperature and the corresponding temperature rise rate are important in defining the potential fire hazard associated with heating of the coals. Typically, the critical self-heating rates under nonadiabatic conditions are of the order of a few Centigrade degrees per minute at the minimum reaction temperature of the coal; they were between ½° and 3° per minute at the AIT's of the finely divided coals in table 7. In comparison, the critical rates are much lower for sustaining an

adiabatic self-heating reaction and usually of the order of a few Centigrade degrees per hour. The values (dT/dt) given in table 6 are less than 10° per hour and refer to the average rate during the first few hours of reaction at the indicated initial temperature. These rates are also indicative of the heat loss rates that could prevent sustained exothermic reaction under non-adiabatic and near-adiabatic heating conditions. In either case, they can be expected to increase with the size of the reacting mass, as predicted by equation 1.

The self-heating hazard in a coal mine may be reduced by increasing the ventilation of a gob area or porous coalbed to prevent any heat accumulation or by reducing the air supply sufficiently to starve the coal of needed oxygen for sustaining an exothermic reaction. Water infusion of a coalbed is another possible control measure that is currently being investigated. Since it is impossible to implement such protection throughout a coal mine, the mining industry should be knowledgeable of the self-heating characteristics of coals and the need for early detection of this hazard.

CONCLUSIONS

The prediction of the spontaneous combustion hazard in coal mines requires a knowledge of incipient combustion criteria and the effects of the properties of the coal, geological features of the coal seam, and the conditions or practices employed in mining. Laboratory-scale studies, such as those of this work, are useful in developing chemical or thermal criteria for detecting and evaluating this hazard. The most widely used criterion is the CO emission or CO index (ppm CO/vol-pct ΔO_2), but it is important to know that all coals can form CO at near-ambient temperature without necessarily any self-heating. Furthermore, any application of these guidelines to the mining environment requires consideration of the many ventilation networks, coalbed variations, and other factors that complicate the scaling. The main conclusions from the present desorption and self-heating experiments are summarized as follows:

1. The CO emission and CO index measured in a closed system increase with decreasing coal rank and are greatest for western coals. They are greatest for dried coal samples, indicating the increased hazard associated with "weathering," and tend to increase with increasing oxygen content of the particular class of coal. At normal ambient temperature, the CO index of finely divided dried coals ranged between 50 to 300 for the bituminous, subbituminous and lignite grades under sealed conditions; corresponding values for undried coals were between 20 and 250.

2. In a mining environment, the CO and CO index can be an order of magnitude or so less than the closed vessel laboratory values because of the excessive dilution and complicated ventilation possible in a mine. Laboratory constant-volume values should correlate best with those for sealed mine atmospheres but the problem of CO loss with wet coals is not well understood.

3. The CO index is sensitive to temperature and, therefore, may be used to indicate the temperature of the reacting coal. However, isotopic tracer experiments have shown little evidence of oxidation for at least the bituminous coals up to about 50° C; decarbonylation or decarboxylation products from previous reaction of the coals appeared to account for the desorption products at near-ambient temperature. Therefore, the presence of small concentrations of CO in a coal mine should not be always assumed as an absolute indicator of spontaneous combustion.

4. The O₂ absorption rate of a coal can also be used as a criterion of spontaneous combustion and does not require any knowledge of the oxidation products. However, the extrapolation of any laboratory rate data to a mining situation involves much greater uncertainties than the use of the CO index.

5. The self-heating temperatures of the coals decrease with decreasing rank, consistent with the CO, CO index, and ΔO_2 rate data, and are lowest when the coals are predried and exposed to moist air. The critical temperatures for sustaining an exothermic reaction are at least 60° C for the bituminous coals and as low as 30° C for most of the lignite or subbituminous coals.

6. The heat-of-wetting appears to be sufficient to initiate self-heating of the lower ranked coals at near-ambient temperature. These coals do not display such a marked temperature dependence for their oxidation rate as do the less reactive coals. Humidity or moisture effects are minimal for the bituminous coals that have relatively high self-heating temperatures.

7. Spontaneous combustion susceptibility of the coals increases with decreasing methane content, which could conceivably pose a problem in mines where methane drainage is being used to minimize the gaseous explosion hazard.

8. The fire hazard may be reduced by sealing the reacting coalbed or gob area to eliminate the oxygen supply, ventilating the coalbed to prevent accumulation of heat, or by injecting water to provide sufficient cooling. Early detection of any self-heating is necessary because of the practical limitations of applying the above protective measures if the self-heating mass is very large or if its temperature is beyond control.

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